Engin.
rary

FEB 11 1932

U. S. DEPARTMENT OF COMMERCE

BUREAU OF STANDARDS JOURNAL OF RESEARCH

Vol. 8 JANUARY, 1932 No. 1

CONTENTS

RP. No.	TITLE AND AUTHOR	Page
396.	The preparation of crystalline methyl-*d*-gulosides by means of coordination compounds with calcium chloride. Horace S. Isbell	1
397.	International comparison of X-ray standards. Lauriston S. Taylor	9
398.	Volumetric determination of pentoses and pentosans. G. M. Kline and S. F. Acree	25
399.	A method for determining the volume changes occurring in metals during casting. C. M. Saeger, jr., and Eugene J. Ash	37
400.	Registration of cathode rays by thin films of metals and metal compounds. Warren W. Nicholas and C. G. Malmberg	61
401.	Effect of casting temperature and of additions of iron on bearing bronze (Cu 80:Sn 10:Pb 10). C. E. Eggenschwiller	67
402.	Ultrasonic measurements of the compressibility of solutions and of solid particles in suspension. Chester R. Randell	79
403.	On elimination of liquid potentials with potassium chloride and ammonium chloride. G. M. Kline, M. R. Meacham, and S. F. Acree	101
404.	An electrostatic voltmeter. Warren W. Nicholas	111
405.	The heats of combustion of methyl and ethyl alcohols. Frederick D. Rossini	119
406.	A clock-controlled constant-frequency generator. A. B. Lewis	141

BUREAU OF STANDARDS JOURNAL OF RESEARCH

CONTENTS OF RECENT NUMBERS

August, 1931 (Vol. 7, No. 2)

RP339. A new apparatus for preparing Ra B+C sources. L. F. Curtiss. Price, 5 cents.

RP340. The photographic emulsion: After-ripening. Burt H. Carroll and Donald Hubbard. Price, 10 cents.

RP341. A simultaneous radiotelephone and visual range beacon for the airways. F. G. Kear and G. H. Wintermute. Price, 20 cents.

RP342. Design of standards of inductance, and the proposed use of models in the design of air-core and iron-core reactors. H. B. Brooks. Price, 15 cents.

RP343. The heat of formation of water and the heats of combustion of methane and carbon monoxide. A correction. Frederick D. Rossini. Price, 5 cents.

RP344. Elastic problem of a wire-wound cylinder. Chester Snow. Price, 10 cents.

RP345. The restoration of solarized ultra-violet transmitting glasses by heat treatment. A. Q. Tool and R. Stair. Price, 10 cents.

RP346. The determination of oxygen and nitrogen in irons and steels by the vacuum-fusion method. H. C. Vacher and Louis Jordon. Price, 10 cents.

RP347. Some electrical properties of foreign and domestic micas, and the effect of elevated temperatures on micas. A. B. Lewis, E. L. Hall, and Frank Caldwell. Price, 10 cents.

September, 1931 (Vol. 7, No. 3)

RP348. The resistance to wear of carbon steels. Samuel J. Rosenberg.

RP349. Permanence studies of current commercial book papers. John O. Burton.

RP350. Thermomagnetic investigation of tempering of quenched 0.75 per cent carbon steel. George A. Ellinger.

RP351. Hyperfine structures in the first spectra of krypton and xenon. C. J. Humphreys.

RP352. Accelerated aging test for paper. Royal H. Rasch. Price, 10 cents.

RP353. Cryoscopic constant, heat of fusion, and heat capacity of camphor. Mikkel Frandsen.

RP354. The passage of gas through the walls of pyrometer protection tubes at high temperatures. Wm. F. Roeser.

RP355. An experimental study of several methods of representing photographic sensitivity. Raymond Davis and Gerald Kent Neeland.

RP356. Some experimental studies of the vibrations of quartz plates. R. B. Wright and D. M. Stuart.

RP357. Aqueous solutions of ethylene, glycol, glycerin, and sodium silicate as quenching media for steels. T. E. Hamill.

RP358. Optical rotation and atomic dimensions—halogeno-tetra acetyl derivatives of manose. Their configurational peculiarities. D. H. Brauns.

RP359. Soil-corrosion studies: Nonferrous metals and alloys, metallic coatings, and specially prepared ferrous pipes removed in 1930. K. H. Logan.

RP360. Isolation and determination of the cyclohexane in a midcontinent petroleum. Johannes H. Bruun and Mildred M. Hicks-Bruun.

October, 1931 (Vol. 7, No. 4)

RP361. Relation between the twist and certain properties of rayon yarns. Homer A. Hamm and Richard S. Cleveland.

RP362. The hydrolysis of chestnut and quebracho tanned leathers by sulphuric acid. E. L. Wallace.

RP363. Correlation of certain soil characteristics with pipe line corrosion. I. A. Denison.

RP364. Further description and analysis of the first spectrum of krypton. Wm. F. Meggers, T. L. deBruin, and C. J. Humphreys.

Research papers, where price is given, are already available, and others will be available in the near future, as separates for purchase from the Superintendent of Documents, United States Government Printing Office, Washington, D. C.

U. S. DEPARTMENT OF COMMERCE
R. P. LAMONT, Secretary
BUREAU OF STANDARDS
GEORGE K. BURGESS, Director

BUREAU OF STANDARDS JOURNAL OF RESEARCH

January, 1932
Vol. 8, No. 1

UNITED STATES
GOVERNMENT PRINTING OFFICE
WASHINGTON : 1932

For sale by the Superintendent of Documents, Washington, D. C. - Price 40 cents; $3 Per Year on Subscription

For a partial list of previous research papers appearing in BUREAU OF STANDARDS JOURNAL OF RESEARCH see pages 2 and 3 of the cover

THE PREPARATION OF CRYSTALLINE METHYL-*d*-GULOSIDES BY MEANS OF COORDINATION COMPOUNDS WITH CALCIUM CHLORIDE [1]

By Horace S. Isbell

ABSTRACT

The reaction between reducing sugars and methyl alcohol in the presence of hydrogen chloride gives a mixture of isomeric methyl glycosides. Frequently amorphous products are obtained which can not be brought to crystallization by the usual methods. The separation of two isomeric methyl gulosides from such a mixture was accomplished by means of crystalline coordination compounds with calcium chloride. So far as known these compounds are the first of this type to be prepared from the methyl glycosides. The calcium chloride was removed by means of silver oxalate, and crystalline α-methyl-*d*-guloside (monohydrate) and β-methyl-*d*-guloside were obtained for the first time.

The new α-and β-methyl-*d*-gulosides were acetylated and the crystalline tetra-acetyl-α-and β-methyl-*d*-gulosides were obtained for the first time. The optical rotations of these compounds are compared with the rotations of the corresponding derivatives of glucose, galactose, and mannose.

CONTENTS

	Page
I. Introduction	1
II. The preparation and properties of calcium chloride methyl gulosides	2
III. Tetra-acetyl-methyl-*d*-gulosides	4
IV. Experimental details	5
1. α-Methyl-*d*-guloside $CaCl_2.2H_2O$	5
2. (α-Methyl-*d*-guloside)$_2$ $CaCl_2.3H_2O$	5
3. α-Methyl-*d*-guloside H_2O	6
4. β-Methyl-*d*-guloside $CaCl_2.2H_2O$	6
5. (β-Methyl-*d*-guloside)$_2$ $CaCl_2$	7
6. β-Methyl-*d*-guloside	7
7. Tetra-acetyl-α-methyl-*d*-guloside	7
8. Tetra-acetyl-β-methyl-*d*-guloside	8
V. Summary	8
VI. Acknowledgment	8

I. INTRODUCTION

In 1893 Emil Fischer [2] discovered that two isomeric methyl glucosides are formed from glucose by the action of methyl alcohol in the presence of hydrochloric acid. Subsequently Fischer's method has been applied to other sugars giving many similar compounds. The reaction yields a mixture of glycosides from which crystalline products can not always be obtained. These mixtures are very complex, probably containing many substances, the separation of which is very desirable. Since in the aldohexose series only methyl glycosides of glucose, galactose,[3] and mannose [4] were known in the crystalline state, the preparation of additional methyl glycosides was undertaken.

[1] An abstract of this paper was read before the National Academy of Sciences in September, 1930 (Proc. Nat. Acad. Sci., vol. 16, p. 699).
[2] Fischer, Ber., vol. 26, p. 2400; 1893.
[3] Fischer and Beensch, Ber., vol. 27, p. 2480; 1894.
[4] Fischer, Ber., vol. 26, p. 2401; 1893; Haworth and Porter, J. Chem. Soc., p. 649; 1930.

Recently the writer [5] found a new calcium chloride compound of *d*-gulose which makes available a crystalline derivative of that sugar. The new compound may be used as a raw material for the preparation of other derivatives. The synthesis of the methyl gulosides was first attempted by Blanksma and Van Ekenstein [6] who obtained a sirup which they were unable to bring to crystallization. The writer has repeated their work, starting with pure gulose which was prepared by removing the calcium chloride from α-*d*-gulose $CaCl_2.H_2O$ with silver oxalate. A relatively pure product was obtained, but it could not be brought to crystallization and, after a through trial, it was evident that a new method was necessary to reach the desired substance. Although crystalline calcium chloride compounds of the glycosides were unknown, the encouraging results obtained by the application of the calcium chloride compounds in the preparation of *d*-gulose, a sugar which had not been previously crystallized, led the writer to apply the same principle in the separation of the methyl gulosides. This resulted in the preparation of crystalline calcium chloride compounds of α- and β-methyl-*d*-gulosides. These compounds served for the separation of the α- and β-isomers from the complex reaction product and ultimately gave the pure methyl gulosides in the crystalline state.

II. THE PREPARATION AND PROPERTIES OF CALCIUM CHLORIDE METHYL GULOSIDES

The calcium chloride methyl gulosides were first prepared by the addition of calcium chloride to the gulose sirup obtained by the method of Blanksma and Van Ekenstein. Subsequently, the method was simplified by preparing the calcium chloride gulosides direct from *d*-gulose calcium chloride in the following manner: The calcium chloride compound was refluxed with methyl alcohol containing about 1 per cent hydrogen chloride. After several hours an excess of powdered calcium carbonate was added; the hydrochloric acid was neutralized, forming calcium chloride. This additional salt did not interfere appreciably with the crystallization of the calcium chloride methyl gulosides which were easily obtained upon evaporation of the solution. The first crystals separated in slender needle-like prisms which gave a specific rotation of about $+60°$. The analysis corresponds to the formula: α-methyl-*d*-guloside.$CaCl_2.2H_2O$. In the preliminary work the calcium chloride was removed from this crude product by means of silver oxalate. After considerable difficulty a crystalline product was obtained from the resulting solution which, after drying in vacuo over P_2O_5, gave the correct analysis for a methyl guloside. Its specific rotation, $+106°$, was commensurate with the value derived from the calcium chloride compound from which it was prepared, and the molecular rotation (20,600) differed normally from the molecular rotation ($-16{,}100$) of β-methyl-*d*-guloside.

Previously [7] these observations were considered as evidence that the substance was pure and that the molecular rotation of α-methyl-*d*-guloside was $+20{,}600$. Subsequent work, however, has shown that the product first obtained was not strictly pure and the value is somewhat low. The pure guloside is best prepared from a second calcium

[5] Isbell, B. S. Jour. Research, vol. 5, (RP226), p. 741; 1930.
[6] Blanksma and Van Ekenstein, Chemisch Weekblad, vol. 5, p. 777; 1908.
[7] Isbell, B. S. Jour. Research, vol. 3, (RP128), p. 1041; 1929.

chloride compound (α-methyl-*d*-guloside)$_2$ $CaCl_2.3H_2O$, which is obtained by the addition of ethyl alcohol to a hot aqueous solution of the calcium chloride compound mentioned above. After several crystallizations from aqueous ethyl alcohol, it gave $[\alpha]_D^{20} = +83$, which corresponds to a somewhat higher molecular rotation than that obtained from the parent substance. The pure guloside is readily obtained from this product by removing the calcium chloride with silver oxalate. It crystallizes from aqueous solution with 1 molecule of water of crystallization. The specific rotation of the monohydrate (+109) is in accord with the value obtained from (α-methyl-*d*-guloside)$_2$ $CaCl_2.3H_2O$. The molecular rotation (23,100) differs from the molecular rotation of β-methyl-*d*-guloside (−16,100) by 39,200 which is slightly more than the value reported by Hudson for the methyl glucosides (37,460) and galactosides (37,900). The question remained whether the first calcium chloride compound constituted a different form of the guloside or whether it contained some impurity which lowered its rotation. This was answered by the preparation of both calcium chloride compounds from pure α-methyl-*d*-guloside (monohydrate). The first compound was obtained by adding an excess of calcium chloride, while the second compound was obtained by using the calculated amount of the salt. The specific rotation of the first compound (α-methyl-*d*-guloside $CaCl_2.2H_2O$) when prepared from the pure guloside is +67°. This is equivalent to a molecular rotation of 22,900 which is in accord with the values 23,100 and 23,000 obtained from α-methyl-*d*-guloside monohydrate and (α-methyl-*d*-guloside)$_2$ $CaCl_2.3H_2O$, respectively.

The mother liquor from the preparation of the calcium compounds just described gave, on standing, a third calcium chloride methyl guloside. The substance separates in rectangular prisms which are moderately soluble in ethyl alcohol. The analysis corresponds to the formula β-methyl-*d*-guloside $CaCl_2.2H_2O$. It melts at 155° and gives a specific rotation of −46°. Upon recrystallization from hot absolute ethyl alcohol this compound changes into a fourth calcium chloride methyl guloside which separates in small, poorly defined crystals. It is easily obtained pure because it is very insoluble in absolute ethyl alcohol. It gives a specific rotation of −65° and the analysis corresponds to the formula (β-methyl-*d*-guloside)$_2$ $CaCl_2$. After removing the calcium chloride with silver oxalate β-methyl-*d*-guloside is easily obtained in the crystalline state. It separates in well-defined truncated prisms which melt at 176° (uncorrected) and give a specific rotation of −83°. This value is equivalent to a molecular rotation of −16,100 which is in agreement with the equivalent rotation −16,200 of the parent calcium chloride compound.

The calcium chloride gulosides are particularly well suited for the study of the equilibria which exist in calcium chloride solutions. In a previous publication [8] it was shown that calcium chloride alters the composition of a solution of *d*-gulose by combining selectively with the alpha form of the sugar. The behavior of the methyl gulosides further illustrates the difference in the stability of the calcium chloride compounds of isomeric substances. Thus α-methyl-*d*-guloside $CaCl_2\,2H_2O$ on crystallization from aqueous alcohol is converted into (α-methyl-*d*-guloside)$_2$ $CaCl_2.3H_2O$, which may be recrystallized from water without decomposition. β-Methyl-*d*-guloside $CaCl_2.2H_2O$

[8] Isbell, B. S. Jour. Research, vol. 5, (RP226), p. 748; 1930.

on crystallization from alcohol is converted into (β-methyl-*d*-guloside)$_2$ $CaCl_2$. In contrast to the alpha isomer this compound is dissociated in water and pure β-methyl-*d*-guloside may be crystallized from the aqueous solution. The solvent and the concentration of calcium chloride are important factors in determining the solubility and stability of such compounds.

The method for the separation of the methyl gulosides which has been described may be applicable for the separation of other glycosides as yet unknown in the crystalline state. It is not to be expected that glycosides of all sugars will form crystalline compounds with calcium chloride or other salts. However, a number of compounds of this type have already been prepared and undoubtedly many more will be found in the future.

III. TETRA-ACETYL-METHYL-*d*-GULOSIDES

As pointed out in a previous publication [9] the optical rotations of the methyl gulosides are of particular importance in regard to the relation between optical rotation and stereomeric configuration. In this respect the rotations of acetyl derivatives are only slightly less important; consequently the alpha and beta methyl gulosides were acetylated and the corresponding acetyl derivatives were prepared.

The new compounds are crystalline substances which resemble the acetylated methyl glucosides. Tetra-acetyl-α-methyl-*d*-guloside gives $[\alpha]_D^{20} = 97.3$ which is equivalent to a molecular rotation of 35,200, while tetra-acetyl-β-methyl-*d*-guloside gives $[\alpha]_D^{20} = -32.1$ which is equivalent to a molecular rotation of $-11{,}600$. The difference in the molecular rotations of these alpha and beta isomers is 46,800. This value is considerably less than the "normal" value, obtained by Dale and Hudson [10] from the corresponding derivatives of glucose (53,900) and galactose (53,460); nevertheless it is considerably greater than the values obtained from the corresponding derivatives of mannose [11] (34,600) and 4-glucosido-mannose [12] (34,130). In a previous publication [12] it was clearly shown that certain derivatives of 4-glucosido-mannose give abnormal rotations, and since 4-glucosido-mannose can not form a 1, 4 ring, these exceptional rotations are not caused by that structure. The existence of numerous instances, wherein it may be shown that combination occurs between sugar derivatives and the solvent or added substances, such as calcium chloride, shows that sugar solutions are extremely complex. The stability of many of the coordination compounds, such as the calcium chloride compounds of *d*-gulose depends largely on the stereomeric structure of the substance and the solvent employed. Likewise one would expect that intermolecular combination with possible distortion and change in optical rotation would be influenced by the stereomeric configuration and the solvent. The effect of these factors on the comparative optical rotations of the sugar derivatives is largely a matter of speculation; but, regardless of the interpretation, the data at hand appear to indicate that only substances of closely related structure invariably give like constants, whereas substances of widely different configuration frequently give exceptional values.

[9] Isbell, B. S. Jour. Research, vol. 3, (RP123), p. 1041; 1929.
[10] Dale and Hudson, J. Am. Chem. Soc., vol. 52, p. 2534; 1930.
[11] Dale, J. Am. Chem. Soc., vol. 46, p. 1046; 1924.
[12] Isbell, B. S. Jour. Research, vol. 7, (RP392), p. 1115; 1931.

IV. EXPERIMENTAL DETAILS

1. α-METHYL-*d*-GULOSIDE $CaCl_2.2H_2O$

Forty grams of α-*d*-gulose $CaCl_2.H_2O$ was refluxed six hours with 300 ml of absolute methyl alcohol containing 4.5 g of anhydrous hydrogen chloride. The warm solution was cautiously neutralized with finely powdered calcium carbonate using a slight excess. After the addition of about 1 g of decolorizing charcoal the solution was filtered. The filtrate was concentrated in vacuo to a thick sirup which was transferred to a beaker using about 50 ml of absolute ethyl alcohol. In the course of several hours long slender needlelike crystals began to form. After 24 hours the crystals were collected upon a filter and washed with a mixture of equal parts of absolute ethyl alcohol and ethyl acetate. The mother liquor was evaporated in vacuo to a thick sirup which was then saturated with ethyl acetate, and a second crop of crystals was obtained. By evaporating the mother liquor more crystalline material was obtained. The first crop weighed 15 g, $[\alpha]_D^{20} = +60.8$; the second, 3.72 g, $[\alpha]_D^{20} = +37.5$; the third, 6.0 g, $[\alpha]_D^{20} = +17.3$; the fourth, 3.5 g, $[\alpha]_D^{20} = -36.0$. The second and third fractions were recrystallized, giving 5 g of product, $[\alpha]_D^{20} = +59.7$, which was added to the first fraction. The combined product which gave a specific rotation of about +60 was dried at 40° C. and subsequently analyzed. The analysis (Ca, 11.67; Cl, 20.67) corresponded to the formula $C_7H_{14}O_6$ $CaCl_2.2H_2O$, but the molecular rotation ($60 \times 341 = 20{,}460$) is less than that obtained from the product prepared by the addition of calcium chloride to pure α-methyl-*d*-guloside (monohydrate). The specific rotation (+67) of the synthetic product indicates that the first preparation contained some impurity (probably β-methyl-*d*-guloside $CaCl_2.2H_2O$) which lowered its rotation.

Three grams of α-methyl-*d*-guloside.H_2O were dissolved in a few milliliters of water and 3 g of $CaCl_2$ were added. After standing several days in a desiccator a crystalline product was obtained which was collected upon a filter and thoroughly washed with 95 per cent ethyl alcohol. The crystals are like those of the calcium chloride derivative first obtained. They are very faintly double refracting and appear as slender pointed prisms which melt at 185° to 190°. *Analysis calculated for* $C_7H_{14}O_6$ $CaCl_2.2H_2O$: Ca, 11.75; Cl, 20.79. *Found*: Ca, 11.54; Cl, 20.77. $[\alpha]_D^{20} = +66.8$ in water (0.7474 g α-methyl-*d*-guloside $CaCl_2.2H_2O$ dissolved in 20 ml read 14.42° S. in a 2 dm tube). The substance is very soluble in water and methyl alcohol, less soluble in ethyl alcohol, and nearly insoluble in ether. It changes on crystallization from ethyl alcohol into a second derivative which is described in the next paragraph.

2. (α-METHYL-*d*-GULOSIDE)$_2$ $CaCl_2 . 3H_2O$

This substance was obtained from α-methyl-*d*-guloside $CaCl_2.2H_2O$ by crystallization from ethyl alcohol and water. About 15 g of α-methyl-*d*-guloside $CaCl_2.2H_2O$ was dissolved in a small amount of hot water (10 ml) and about 200 ml of absolute ethyl alcohol were added. After a few minutes, strongly double-refracting, short prismatic crystals began to separate and soon thereafter some needlelike faintly double-refracting crystals also began to form. The crystals were then separated and recrystallized. After a number of crystal-

lizations a homogenous product was obtained, which was not changed by recrystallization from water or alcohol. The new substance is very soluble in water, and methyl alcohol, but difficultly soluble in ethyl alcohol. For analysis the product, which contains three molecules of water of crystallization, was air-dried at 40° C. It gives up its water of crystallization at 100° in vacuo; the anhydrous material absorbs moisture very rapidly but the hydrate is not hygroscopic. The anhydrous material melts with decomposition at about 215° C. The melting point of the hydrate depends upon the rate of heating; when heated slowly it melts with decomposition at about 205°, but when placed in a hot bath it melts at as low as 170° C. *Analysis calculated for* $(C_7H_{14}O_6)_2\ CaCl_2.3H_2O$: C, 30.37; H, 6.19; Ca, 7.24; Cl, 12.82. *Found*: C, 30.46; H, 6.35; Ca, 7.23; Cl, 12.83. *Loss on drying three hours at 100° C. in vacuo*: Subs., 0.7889; loss, 0.0755. *Calculated for 3 molecules of water*: 0.0771. $[\alpha]_D^{20} = +82.8$ in water (0.8671 g in 25 ml read 16.58° S. in a 2 dm tube, $[\alpha]_D^{20} = +82.75$; 0.1980 g in 25 ml read 7.58° S. in a 4 dm tube, $[\alpha]_D^{20} = +82.83$).

3. α-METHYL-*d*-GULOSIDE H_2O

About 10 g of (α-methyl-*d*-guloside)$_2$ $CaCl_2.3H_2O$ was shaken with about 15 g of freshly prepared silver oxalate. The insoluble calcium and silver salts were separated, leaving a relatively pure solution of α-methyl-*d*-guloside. This was evaporated in vacuo to a thick sirup which was diluted somewhat with ethyl alcohol and saturated with ether. The solution was allowed to stand in the ice box. After several days a crystalline product separated. The new substance crystallizes in thin plates which frequently appear hexagonal. It is very soluble in water and ethyl alcohol but difficultly soluble in ether. It melts at 77° C. losing its water of crystallization. The hydrate is not hygroscopic, but the anhydrous material readily absorbs water. It has a sweet taste. For analysis the substance was dried at 35° to 40° C. in air. After one crystallization the specific rotation in water was +108.8; after a second crystallization $[\alpha]_D^{20} = +109.4$ (0.5166 g of α-methyl-*d*-guloside.H_2O dissolved in 25 ml read 13.06° S. in a 2 dm tube). *Analysis calculated for* $C_7H_{14}O_6.H_2O$: C, 39.60; H, 7.60. *Found:* C, 39.62; H, 7.75. *Loss on drying three hours at 100° C. in vacuo:* Subs., 1.8208; loss, 0.1545. Calculated for one molecule of water, 0.1546.

4. β-METHYL-*d*-GULOSIDE $CaCl_2.2H_2O$

This substance is obtained from the residue which remains after separating the positively rotating calcium chloride methyl gulosides. The fraction which gave a specific rotation of −36 was recrystallized from aqueous alcohol. β-methyl-*d*-guloside $CaCl_2.2H_2O$ separates in needlelike crystals which on further growth appear as slender rectangular prisms. It melts at 155° C. The new substance is very soluble in water and methyl alcohol, less soluble in ethyl alcohol, and insoluble in ether. *Analysis calculated for* $C_7H_{14}O_6.CaCl_2.2H_2O$: Ca, 11.75; Cl, 20.79. *Found:* Ca, 11.87; Cl, 20.85.C $[\alpha]_D^{20} = -45.7$ in water (0.3695 g dissolved in 25 ml read −3.9° S. in a 2 dm tube.)

On recrystallization from absolute alcohol it loses calcium chloride, forming (β-methyl-*d*-guloside)$_2$ $CaCl_2$. However, it may be crystallized without decomposition from alcohol containing a small quantity of calcium chloride.

5. (β-METHYL-*d*-GULOSIDE)$_2$ $CaCl_2$

A solution of β-methyl-*d*-guloside $CaCl_2.2H_2O$ in absolute ethyl alcohol decomposes on warming, giving (β-methyl-*d*-guloside)$_2$ $CaCl_2$. This substance separates as a fine crystalline precipitate which is almost insoluble in absolute ethyl alcohol. It melts with decomposition at 238° C. (uncorrected) and gives the following analysis: *Analysis calculated for* $(C_7H_{14}O_6)_2$ $CaCl_2$: Ca, 8.03; Cl, 14.21. *Found:* Ca, 8.01, Cl, 14.14. $[\alpha]_D^{20} = -64.9$ in water (0.6669 g (β-methyl-*d*-guloside)$_2$ $CaCl_2$ dissolved in 25 ml read −10.0° S. in a 2 dm tube).

The new substance is very soluble in water, less soluble in methyl alcohol, and nearly insoluble in absolute ethyl alcohol and ether. As shown in the next paragraph, methyl alcoholic and aqueous solutions give on evaporaton β-methyl-*d*-guloside rather than the original material.

6. β-METHYL-*d*-GULOSIDE

β-Methyl-*d*-guloside is obtained from (β-methyl-*d*-guloside)$_2$ $CaCl_2$ by crystallization from water or methyl alcohol. The salt is dissolved in a small quantity of hot water; on cooling, β-methyl-*d*-guloside separates in beautiful prismatic crystals. A portion of the β-methyl-*d*-guloside, however, remains in solution, probably combined with the calcium chloride which results from the dissociation of the original compound. This residual methyl guloside is easily crystallized after the calcium chloride is removed by silver oxalate and a nearly quantitative yield of β-methyl-*d*-guloside is thus obtained. This new glycoside melts at 176° (uncorrected). It tastes slightly sweet. It is fairly soluble in water and methyl alcohol, less soluble in ethyl alcohol, and nearly insoluble in ether. For analysis it was recrystallized from ethyl alcohol and dried at 60° C. in vacuo. *Analysis calculated for* $C_7H_{14}O_6$: C, 43.27; H, 7.27. *Found:* C, 42.92; H, 7.27. $[\alpha]_D^{20} = -83.32$ in water (0.7297 g of β-methyl-*d*-guloside dissolved in 25 ml read −28.1° S. in a 4 dm tube).

7. TETRA-ACETYL-α-METHYL-*d*-GULOSIDE

One gram of α-methyl-*d*-guloside monohydrate was dissolved in a mixture of 7 ml of acetic anhydride and 4 ml of pyridine. After standing 24 hours the solution was poured in ice water and the product was extracted with chloroform. The chloroform solution was washed successively with cold dilute sulphuric acid, sodium bicarbonate, and water. On evaporation it gave 1.6 g of crude crystalline tetra-acetyl-α-methyl-*d*-guloside. The substance separates in irregular clusters of slender crystals which frequently become wider and more prismatic. It is somewhat soluble in water, easily soluble in alcohol, ether, and chloroform. It melts at 98° and tastes slightly bitter. After one crystallization from hot water, $[\alpha]_D^{20}$ (in chloroform) = +96.8; after two crystallizations, $[\alpha]_D^{20} = +97.3$; after three crystallizations, $[\alpha]_D^{20} = +97.3$ (0.8054 g of substance dissolved in 25 ml read +18.1° S. in a 2 dm tube). *Analysis calculated for* $C_{15}H_{22}O_{10}$: C, 49.70; H, 6.12. *Found:* C, 49.76; H, 6.17.

8. TETRA-ACETYL-β-METHYL-*d*-GULOSIDE

One gram of β-methyl-*d*-guloside was dissolved in a mixture of 7 ml of acetic anhydride and 4 ml of pyridine. After standing 24 hours the solution was poured in ice water and the product was extracted with chloroform. The chloroform solution was washed successively with cold dilute sulphuric acid, sodium bicarbonate, and water. On evaporation, a colorless sirup was obtained which readily crystallized after the addition of a few drops of ether. The new substance, tetra-acetyl-β-methyl-*d*-guloside weighed 1.55 g, melted at 66° to 67° and in chloroform solution $[\alpha]_D^{20} = -32.0$. After one crystallization from hot water it melted at 67° and in chloroform solution $[\alpha]_D^{20} = -32.1$ (0.7259 g dissolved in 25 ml read −5.39° S. in a 2 dm tube). *Analysis calculated for* $C_{15}H_{22}O_{10}$: C, 49.70; H, 6.12. *Found:* C, 49.81; H, 6.10.

V. SUMMARY[13]

The separation of two crystalline methyl-*d*-gulosides has been accomplished by means of crystalline coordination compounds with calcium chloride. The following new compounds are reported:

α-Methyl-*d*-guloside $CaCl_2.2H_2O$,	$[\alpha]_D^{20} = +66.8$.
(α-Methyl-*d*-guloside)$_2$ $CaCl_2.3H_2O$,	$[\alpha]_D^{20} = +82.8$.
α-Methyl-*d*-guloside $.H_2O$,	$[\alpha]_D^{20} = +109.4$.
α-Methyl-*d*-guloside tetra-acetate,	$[\alpha]_D^{20} = +97.3$.
β-Methyl-*d*-guloside $CaCl_2.2H_2O$,	$[\alpha]_D^{20} = -45.7$.
(β-Methyl-*d*-guloside)$_2$ $CaCl_2$,	$[\alpha]_D^{20} = -64.9$.
β-Methyl-*d*-guloside,	$[\alpha]_D^{20} = -83.3$.
β-Methyl-*d*-guloside tetra-acetate,	$[\alpha]_D^{20} = -32.1$.

VI. ACKNOWLEDGMENT

The writer takes pleasure in expressing his appreciation to F. J. Bates and other members of the polarimetry section of the Bureau of Standards who have given aid and rendered encouragement in the course of the investigation.

WASHINGTON, November 2, 1931.

[13] In addition to the compounds reported in this paper, a new crystalline penta-acetate of *d*-gulose has been prepared by acetylation of α-*d*-gulose $CaCl_2.H_2O$ with acetic anhydride and zinc chloride. The specific rotation of the substance is about 85°. By treating this compound with hydrogen bromide a bromo-acetyl derivative is obtained from which crystalline tetra-acetyl-β-methyl guloside may be prepared by the Königs and Knorr reaction. These products will be the subject of a future publication.

INTERNATIONAL COMPARISON OF X-RAY STANDARDS [1]

By Lauriston S. Taylor

ABSTRACT

Direct comparisons between the X-ray ionization standards of the United States, England, Germany, and France are described. The small guarded field ionization chamber was used as the working standard and transported to the several laboratories. Careful check of the instrument calibration at each laboratory showed no change due to transportation. Complete corrections were made for air absorption, differences in current measurements, and differences between chamber diaphragms. The final agreement between the standards of the United States, England, and Germany was ±0.5 per cent. The ratio between the International Röntgen and Solomon's Unit for hard radiation (H. V. L. greater than 0.75 mm Cu.) was 2.29. As a result of diaphragm discrepancies found in England, a study of diaphragm measurements was made. It was found that the lead diaphragms tended to warp with age rendering difficult and accurate determination of their area. Plug gage and micrometer microscope measurements were averaged for the final results.

CONTENTS

		Page
I.	Introduction	9
II.	Portable X-ray standardization equipment	10
	1. Description of apparatus	10
	2. Accuracy of calibration	12
III.	Comparisons in this country	12
IV.	Comparison with National Physical Laboratory	13
V.	Comparison with Physikalisch-Technische Reichsanstalt	16
VI.	Comparison with French standard	18
VII.	Study of ionization chamber diaphragms	20
VIII.	Conclusion—Joint recommendations of the Bureau of Standards, National Physical Laboratory, Physikalisch-Technische Reichsanstalt and le Service d'Etalonnage de l'Hôpital St. Antoine	23

I. INTRODUCTION

The unit of X-ray quantity known as the Röntgen has within the last few years become very generally used in applied radiology. In the meantime many investigators have studied the problem of devising an equipment which will unambiguously measure an X-ray beam according to the definition of the international Röntgen as proposed by the Second International Congress of Radiology in 1928 [2] and many important features overlooked by the earlier investigators have been brought out.[3] There has at the same time been set up in the national laboratories of England, Germany, and the United States, standard open-air ionization chambers in terms of which dosage meters for the particular country are calibrated.[4 5 6]

[1] Preliminary report read by L. S. Taylor at Third International Congress of Radiology, Paris, July 29 1931.

[2] The Röntgen is defined as "the quantity of X radiation which when the secondary electrons are fully utilized and the wall effect of the chamber is avoided, produces in 1 cubic centimeter of atmospheric air at 0° C. and 760 cm mercury pressure, such a degree of conductivity that one electrostatic unit of charge is measured at saturation current."

[3] See review paper by L. S. Taylor, Radiology, vol. 16, p. 1; 1931.

[4] H. Behnken, Strahlentherapie, vol. 26, p. 79; 1927.

[5] L. S. Taylor, B. S. Jour. Research, vol. 2 (RP56), p. 771; 1929.

[6] G. W. C. Kaye and W. Binks, Brit. J. Rad., vol. 2, p. 553; 1929.

Other countries, not having centralized standardization laboratories have designated certain private or State institutions as recognized custodians of the standard. In France Dr. I. Solomon at l'Hôpital St. Antoine is the official custodian.

Since the different national standards have been designed and constructed independently it is natural to find that no two are exactly alike, even though the basic principles involved in all are the same. On account of these differences the most obvious question was how closely these several standards agreed.

The first attempt at comparison was made in 1927 by Behnken.[7] For this purpose he carried a pair of carefully controlled thimble chambers, which had been calibrated against his standard, to several laboratories for comparison. His results revealed a difference between several American laboratores (not including the Bureau of Standards, since we had no X-ray standardization equipment at that time) and the Physikalische-technischen Reichsanstalt of some ±4 per cent. More recent studies [8 9] have shown that an unambiguous calibration is exceedingly difficult. Behnken's comparison measurements were made with a magnesium thimble chamber which, therefore, had a considerable dependence upon the radiation quality as compared with an open-air ionization chamber. The impossibility of reproducing the necessary radiation qualities in the different laboratories consequently influenced the accuracy of the measurements in an unfavorable way.

It appeared, therefore, that a direct comparison between the standards themselves would be the only reliable method.[10] This has heretofore been practically precluded by the very great weight and size of these open-air standards. The guarded field ionization chamber developed in this laboratory [11 12] appeared, however, to be sufficiently compact to transport, so the bureau arranged for a comparison with with the national laboratories of England and Germany; also with Doctor Solomon's laboratory of France.

II. PORTABLE X-RAY STANDARDIZATION EQUIPMENT

1. DESCRIPTION OF APPARATUS

The working standard used in these comparisons was a small guarded field ionization chamber previously described,[11 12] though some minor modifications from that description were made to facilitate the more ready alignment in the X-ray beam. At the same time, the beam was isolated from the guard wires by reducing their number from 12 to 8, which permitted a spacing of 1.8 cm between the central pair. With the chamber diaphragm of only 0.8 cm diameter there was little likelihood of the beam striking the wires unless the chamber were placed abnormally close to the tube. The change in spacing of the guard wires necessitated, however, a 3 cm increase in the length of the surrounding box to maintain a uniform electric field between the collector plates. To insure ruggedness, the

[7] H. Behnken, Strahlentherapie, vol. 29, p. 192; 1928.
[8] L. S. Taylor and G. Singer, B. S. Jour. Research, vol. 4 (RP169), p. 631; 1930.
[9] L. S. Taylor and G. Singer, Radiology, vol. 15, p. 227; 1930.
[10] L. S. Taylor, Radiology, vol. 14, p. 551; 1930.
[11] L. S. Taylor and G. Singer, B. S. Jour. Research, vol. 5 (RP211), p. 507; 1930.
[12] L. S. Taylor and G. Singer, Radiology, vol. 15, p. 637; 1930.

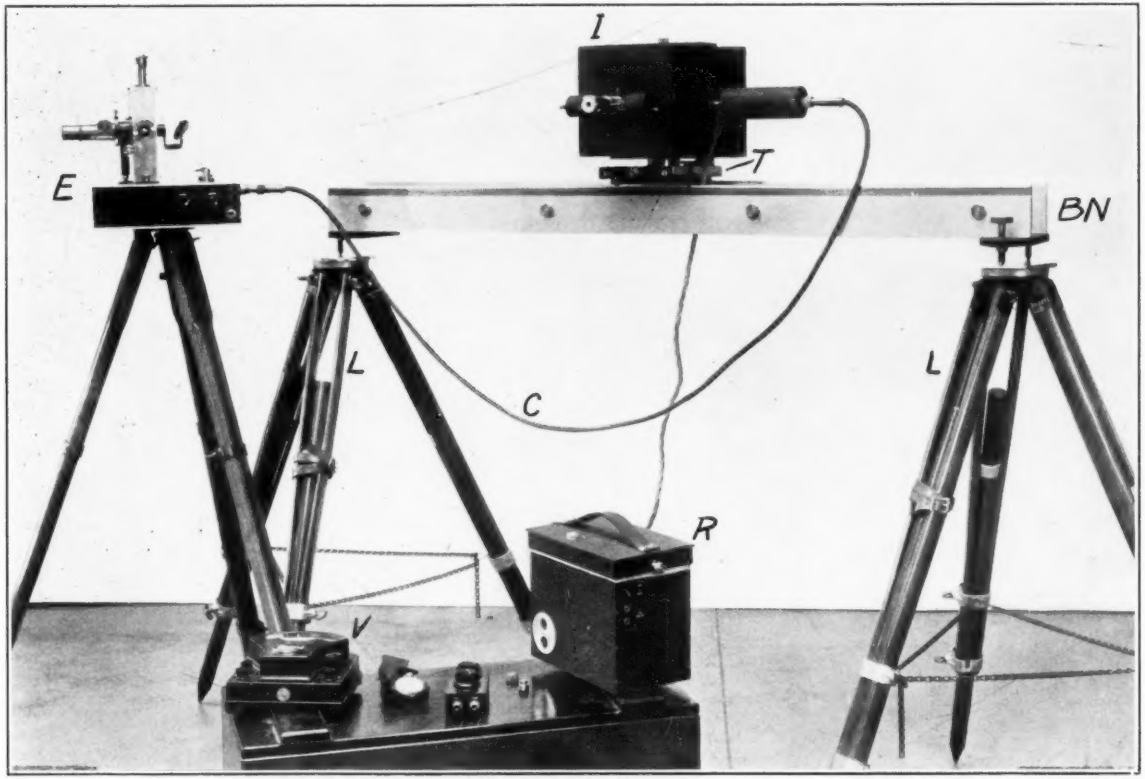

FIGURE 1.—*Photograph of complete X-ray standardization equipment*

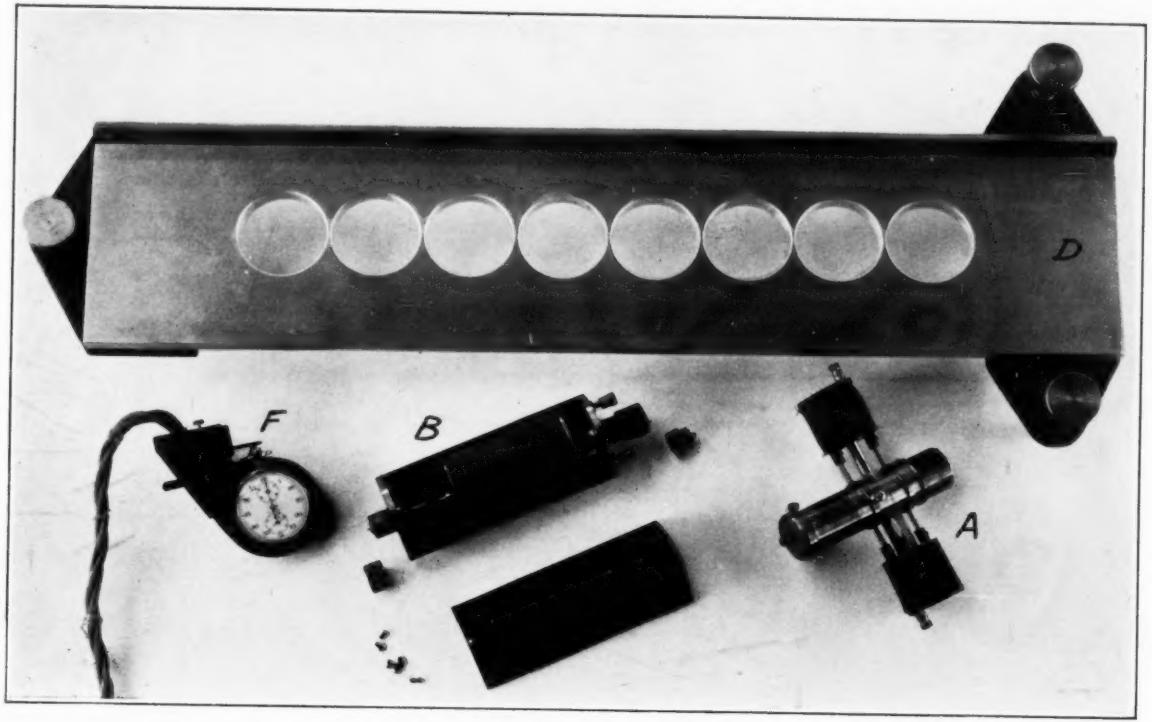

FIGURE 2.—*Accessory equipment*

older potential dividing resistors of carbon were replaced by wire-wound resistors.

The current-measuring system used (*E*, fig. 1) has already been described.[13] [14] In this the electric charge furnished by the ionization chamber is entirely localized in a condenser having one plate connected to the ionization chamber collector electrode and the other to a source of continuously variable potential. The localization is is effected by maintaining the receiving line at a constant potential by properly changing the variable potential. This change in potential measures the accumulated charge. The null reading electrometer is connected to the ionization chamber, *I*, by a flexible rubber cable, *C*, surrounded by an earthed copper sheath. It may be noted that since, in the current measurements, the potential of the system is maintained at zero, cable leakage plays no part in the magnitude, but merely affects the sensitivity.

To derive the current, two different timing devices were used as circumstances demanded. The first was a magnetically operated lead shutter (*A*, fig. 2) to fix the exposure interval to the X-ray beam entering the ionization chamber. The second was a magnetically operated switch, *B*, placed in the electrometer circuit to disconnect the measuring system from the ionization chamber. The second method is less desirable than the first because breaking the connection changes the capacity of the system; this requiring that the electric switch be operated only when the electrometer indicates zero potential, and that no adjustment of the compensator be made after opening the switch.

Both shutter and magnetic switch are operated and timed by means of a combined stop watch and 2-way switch. (*F*, fig. 2.) The switch is adjusted to operate at the instant the stop watch is started and stopped, during which interval the operator balances the ionization current by changing the voltage, *V*, of the compensating condenser. The ratio of the compensating voltage, *V*, to the interval, *t*, is proportional to the ionization current.

Saturation voltage for the ionization chamber was supplied from a compact 2,000-volt kenotron rectifier (*R*, fig. 1), having a filter capacity of 1 μf. The current drawn off by the potential divider for the guard wires, being only 4×10^{-4} amperes, introduces no appreciable ripplage in the saturation voltage.

The ionization chamber was mounted on a swivel table and short cross slide, *T*, for adjustment in a direction at right angles to the beam in the horizontal plane; and the cross slide in turn mounted on an aluminum optical bench, *BN*, for adjustment along the beam. Two such benches were used—one 5 feet long, *B*, and the other about 20 inches (*D*, fig. 2). A pair of rugged adjustable tripods, *L*, were used for supporting the optical benches.

For transportation the entire equipment and a few spare parts were placed in the three cases. The two smaller ones containing the chamber, electrostatic compensator, *E*, and voltmeter, *V*, were carried by hand throughout the journey, while the large one, containing the accessories and 2,000-volt generator, was shipped.

---

[13] L. S. Taylor, B. S. Jour. Research, vol. 6 (RP306), p. 807; 1931.
[14] L. S. Taylor, Radiology, vol. 17, p. 294; 1931.

2. ACCURACY OF CALIBRATION

The accuracy of the compensator depends solely upon the fixed capacity in the compensator case. The calibration of this capacity was checked in each laboratory before using. The values of the calibration constant k_o,[15] as obtained at the various places, are given in Table 1. In addition, a complete calibration of the fixed capacity of the compensator was also carried out in Teddington, giving a value of 828.4 $\mu\mu$f as compared with 828.2 $\mu\mu$f, obtained before leaving and after returning to Washington. In the final calibration, a variable capacity was used with its series of capacity differences accurate to within one-tenth per cent, and no deviation from the mean in any determination exceeded one-tenth per cent.

The voltmeter used for measuring the compensating potential was corrected to one-tenth per cent and a number of checks during the journey indicated that no changes occurred in transit.

TABLE 1.—*Compensator calibration constants (k_o) obtained in different laboratories*

	k_o
Washington (May 1, 1931)	1.045$_2$
Teddington (N. P. L.)	1.045$_7$
Berlin (P. T. R.)	1.045$_4$
Paris (L'Hopital St. Antoine)	1.046$_2$
Washington (Sept. 4, 1931)	1.045$_9$

Our earlier investigations led to a definite set of requirements, which were being adhered to as closely as possible in all comparisons. First, a replacement method of measuring the radiation was chosen, since it eliminates any uncertainty as to quality variations over the area of the beam. Then it was necessary to have the X-ray beam uniform over the area of the chamber diaphragm. Experience has shown that this must be tested for each set-up; visual alignment may lead to error.

Corrections for loss of radiation by absorption in the air between the chamber diaphragm and collector electrode were also considered necessary, though with the guarded field chamber this correction has been reduced to a minimum which is negligible for the highly filtered radiations. With some of the larger air chambers, however, this can not be neglected anywhere within the practical range of wave lengths.

Data for the absorption of heterogeneous radiation in air are very incomplete; hence it was deemed necessary to interpolate between known coefficients for many radiation qualities encountered.[16,17] The values in this work so obtained are probably accurate to within about 15 per cent.

III. COMPARISONS IN THIS COUNTRY

Measurements have been previously described which show an average agreement between the large open-air ionization and the earlier guarded field (12-wire) chamber closer than 0.1 per cent.[18]

[15] k_o is the ratio of the potentials V_o/v_o where v_0 is the potential induced on the insulated system by the application of V_o to the compensator condenser, when all external capacities are removed from the compensator. A determination of k_o serves as a check on the calibration of the capacity.

[16] M. Siegbahn, The Spectroscopy of X Rays, Appendix, Table 3, Oxford University Press; 1925.

[17] L. S. Taylor and G. Singer, B. S. Jour. Research, vol. 6 (RP271), p. 219; 1931.

[18] L. S. Taylor and G. Singer, B. S. Jour. Research, vol. 5 (RP211), p. 507; 1930.

Comparisons between the earlier 12-wire chamber and the present 8-wire chamber showed agreement within 0.2 per cent.

In cooperation with Dr. G. Failla, a comparison of the bureau's current-measuring system with that of Memorial Hospital, of New York,[19] was made, theirs being the only laboratory in this country using null compensation methods. This was primarily to be certain that our system would stand transportation. For comparison the B. S. compensator was simply connected directly to Failla's calibrated radium-ionization chamber. With a steady potential applied to the radium chamber, the resultant current was compensated for a convenient length of time. Measurements over a 20-fold range of current are given in Table 2.

It will be noticed that the small differences are progressive—the radium-compensator readings becoming more negative with respect to bureau readings as smaller currents were used.

TABLE 2.—*Comparison of compensators with Memorial Hospital*

Radium compensator	Electrostatic compensator	Per cent difference	Average deviation, Bureau of Standards
e. s. u.	*e. s. u.*		*Per cent*
13.11	13.18	−0.53	±0.9
1.248	1.242	+.24	±.2
0.597	.593	+.66	±.2
Average		+.12	

IV. COMPARISON WITH NATIONAL PHYSICAL LABORATORY

(With the cooperation of Dr. G. W. C. Kaye and W. Binks)

The new N. P. L. chamber is of the Duane type with a 10 cm plate spacing. A diagram of the set-up for making the comparison is shown in Figure 3. Their X-ray tube, of the Coolidge deep therapy type, was in a horizontal lead box with a limiting diaphragm, *A*, 12 mm in diameter at about 40 cm from the target. The ionization-chamber diaphragm, *B*, was 8 mm in diameter. The collector electrode, *C*, had a nominal effective length of 8 cm and its center was approximately 35 cm from the diaphragm. They used a null electrostatic compensator to measure the ionization current. Both ionization chambers were mounted on a short cross slide, which was in turn mounted on a heavy optical bench. (It happened that the bureau chamber fitted exactly on the N. P. L. track.) The replacement method of observation was used, the two chambers being shifted alternately into position for observation. This distance was so fixed that the front face of the chamber diaphragm was in both cases at the same distance from the target—about 100 cm.

Curve I (fig. 4) shows in arbitrary units the distribution of intensity across the X-ray beam as obtained by moving the chamber across it. It should be pointed out that the relative narrowness of such a peak is largely due to the effective slit width of the chamber diaphragm used to "explore" the beam. Some measurements made with a

[19] G. Failla and P. S. Henshaw, Radiology, vol. 17, p. 1; 1931.

smaller diaphragm indicated a more nearly uniform distribution. In any case both chambers were very sensitive to alignment. The operating position of the chambers in the beam is indicated by the arrow.

The two compensating systems were separately compared by using them alternately to measure the ionization in the N. P. L. chamber while the X-ray output was maintained constant according to meter readings. In this comparison the B. S. instrument read 1.47 per cent higher than that of the N. P. L.

During the comparison of chambers it was found that the chamber diaphragms of the two equipments had different effective areas not accounted for by the difference in their diameter. The N. P. L.

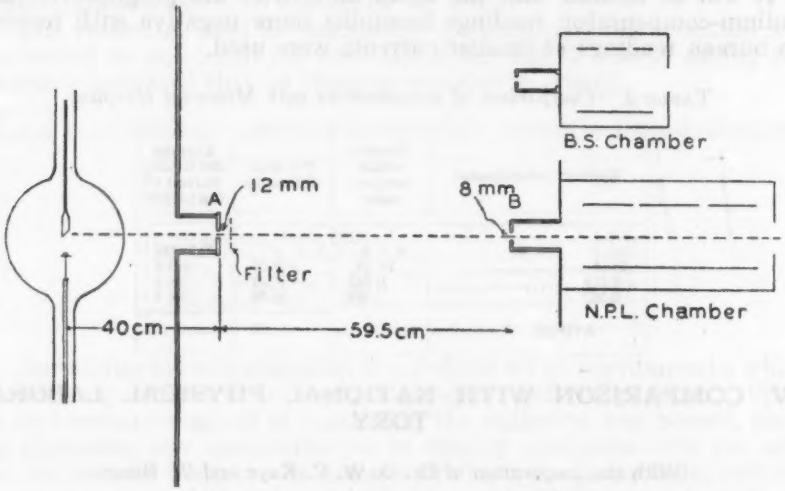

FIGURE 3.—*Diagram of X-ray system in Teddington*

diaphragm was about 9 mm thick and the hole was cylindrical as indicated in Figure 5, *A*. The B. S. diaphragm (*B*, fig. 5) had a taper of 0.02 mm per millimeter length and was only about 4 mm thick along the face of the hole. Depending upon such factors as the focal spot diameter and the distance from target to diaphragm, the two types of diaphragms were found to yield different results. Some measurements made at the same time by the laboratory in Washington, and described below, illustrate this variation.

As dictated by the type of construction, the difference in the distance between the diaphragm and center of the collector for the two chambers amounts to about 15 cm, hence the comparatively soft radiation used necessitated corrections for air absorption. These were obtained by interpolation from previous data.[20]

[20] See footnote 18, p. 12.

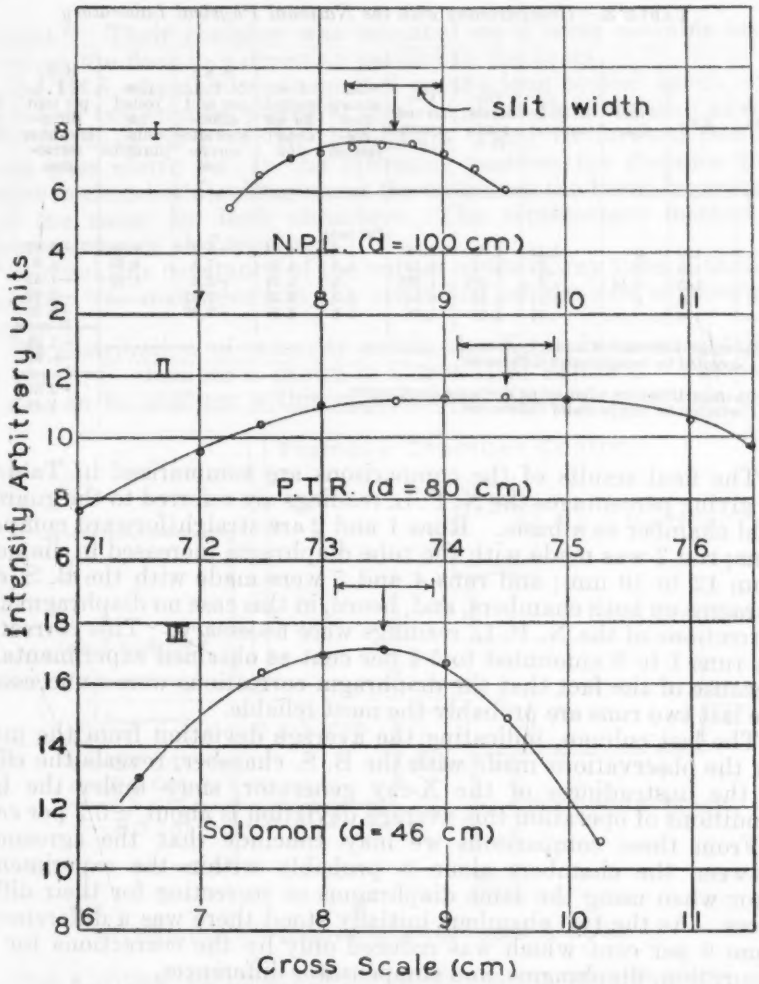

FIGURE 4.—*X-ray intensity distribution across X-ray beams*

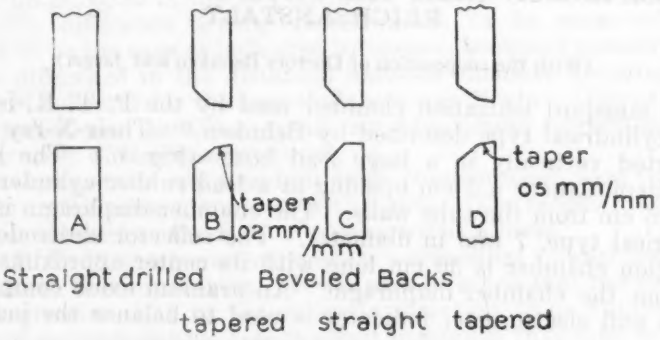

FIGURE 5.—*Types of diaphragms used*

TABLE 3.—*Comparisons with the National Physical Laboratory*

Run	Kv	Filter Cu.	H. V. L. (copper)	Observed r/min B. S.	Observed r/min N. P. L.	Air absorption correction	Corrected for air absorption	B. S./N. P. L. per cent difference after correction	Corrected for diaphragms	B. S./N. P. L. per cent difference after correction	B. S. precision
						Per cent					*Per cent*
1	110	0	0.11	4.30	3.98	1.5	4.04	−6.2	4.26	−0.93	±1.2
2	110	0	.11	4.51	4.13	1.5	4.19	−7.4	4.33	−1.9	±.7
3	143	0.14	.5	1.295	1.205	.6	1.21	−6.4	1.28	−1.32	±.9
4	110	0	.11	4.32	4.14	1.5	4.20	−2.82		−2.82	±1.1
5	110		.11	4.24	4.08	1.5	4.14	−2.39		−2.39	±.8
Average difference of intact systems										−1.38	
Corrected for compensator differences										+.09	
Average difference when using the same diaphragms										−2.61	
Corrected for compensator differences										−1.14	

The final results of the comparisons are summarized in Table 3. In giving percentages the N. P. L. readings are referred to the guarded field chamber as a basis. Runs 1 and 2 are straightforward comparisons; run 3 was made with the tube diaphragm increased in diameter from 12 to 30 mm; and runs 4 and 5 were made with the B. S. diaphragms on both chambers, and, hence, in this case no diaphragm area corrections of the N. P. L. readings were necessary. This correction for runs 1 to 3 amounted to 5.4 per cent as obtained experimentally. Because of the fact that the diaphragm corrections were unnecessary the last two runs are probably the most reliable.

The last column, indicating the average deviation from the mean for the observations made with the B. S. chamber, reveals the effect of the unsteadiness of the X-ray generator, since under the best conditions of operation this average deviation is about ±0.2 per cent.

From these comparisons we may conclude that the agreement between the chambers alone is probably within the experimental error when using the same diaphragms or correcting for their differences. As the two chambers initially stood there was a difference of some 9 per cent which was reduced only by the corrections for air absorption, diaphragms, and compensator differences.

V. COMPARISON WITH THE PHYSIKALISCH-TECHNISCHE REICHSANSTALT

(With the cooperation of Doctors Behnken and Jaeger)

The standard ionization chamber used by the P. T. R. is of the large cylindrical type described by Behnken.[21] Their X-ray tube is supported vertically in a large lead box. (Fig. 6.) The limiting tube diaphragm is a 3 cm opening in a lead rubber cylinder placed about 5 cm from the tube walls. The chamber diaphragm is of the cylindrical type, 7 mm in diameter. The collector electrode of the ionization chamber is 30 cm long with its center approximately 40 cm from the chamber diaphragm. An uranium oxide compensator with a null electrometer indicator is used to balance the ionization

[21] See footnote 4, p. 9.

current.[22] Their chamber was mounted on a table movable on a track on the floor in a direction parallel to the beam.

The B. S. chamber was mounted on the long optical bench, supported on two tripods, placed at right angles to the beam and at such a height that the P. T. R. chamber in taking its forward position could pass above it. In the operating position the distance from target to chamber diaphragm and the section of the beam intercepted was the same for both chambers. The replacement method of observation was also used here.

To check the constancy of the output of the X-ray tube, a thimble chamber was maintained in the beam just off the axis as shown in Figure 6.

The distribution of intensity across the X-ray beam as obtained by the B. S. chamber is shown in Curve II of Figure 4. The beam is seen to be uniform within experimental limits over a wide area,

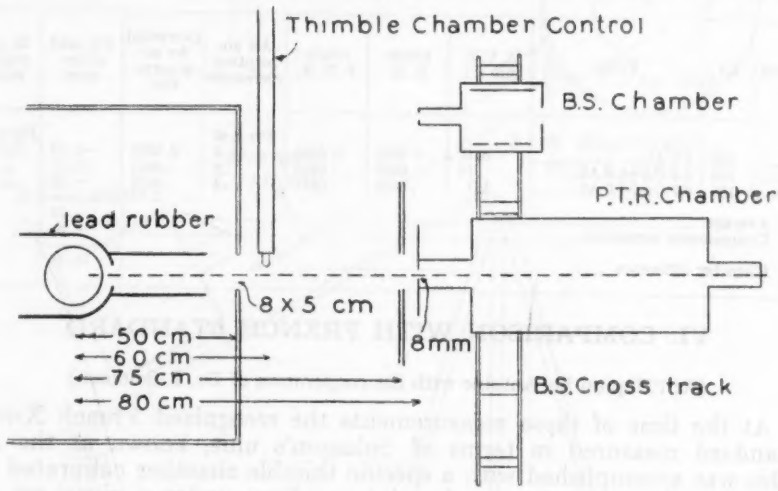

FIGURE 6.—*Diagram of X-ray system in Berlin*

so that a critical alignment of the chambers was not necessary. The working position of both chambers is indicated by the arrows.

The diaphragms of the two chambers had the same thickness, so a negligible difference arising therefrom is to be expected. This proved to be the case as indicated by some subsequent measurements.

The difference in the distances between chamber diaphragm and center of collector for the two chambers was 20 cm. Comparatively hard radiations, entailing small air absorption corrections, were used in most of the measurements.

The electrostatic and uranium oxide compensators were compared directly in the same manner as with Failla. The results are given in Table 4, referred to the B. S. compensator as a basis.

The P. T. R. compensator registers a somewhat smaller magnitude than the B. S. compensator. It will also be noted that the variations are progressive, but in the opposite direction from Failla's. The range of currents in this case is about one-tenth that used in Failla's laboratory.

[22] R. Jaeger, Strahlentherapie, vol. 33, p. 542 1929.

TABLE 4.—*Comparison of compensators at the Physikalisch-Technische Reichsanstalt*

Uranium oxide current amp×10^{-12}	Electrostatic compensator amp×10^{-12}	Difference	Average deviation from mean
		Per cent	*Per cent*
133	134.0	+0.75	±0.31
206	207.1	+.53	±.60
280	281.2	+.43	±.57
Average		+.58	

The comparison as a whole is given in Table 5. The only corrections made were for air absorption in the P. T. R. chamber.

TABLE 5.—*Comparison with the Physikalische-Technischen Reichsanstalt*

Run	Kv	Filter	H. V. L. mm Cu	r/min B. S.	r/min P. T. R.	Air absorption correction	Corrected for air absorption	Per cent difference	B. S. precision
						Per cent			*Per cent*
1	100	2.0 Al	0.16	0.0515	0.0503	1.2	0.0509	−1.17	±0.38
2	150	0.5 Cu+1.0 Al	.75	.0457	.0460	.6	.0463	+1.11	±.5
3	180	0.7 Cu+1.0 Al	1.1	.0476	.0471	.4	.0473	−.68	±.25
Average								−.25	
Compensator correction								+.6	
Chamber difference								+.35	

VI. COMPARISON WITH FRENCH STANDARD

(At l'Hôpital St. Antoine with the cooperation of Dr. I. Solomon)

At the time of these measurements the recognized French X-ray standard measured in terms of Solomon's unit, known as the *R*. This was accomplished with a specific thimble chamber calibrated in terms of the ionization produced by radium under a given set of conditions.[23]

Differences in the apparatus, and the general experimental conditions, necessitated a comparison procedure different from that followed with N. P. L. and P. T. R. A fairly broad X-ray beam was used as a source, and measurements made with the two chambers simultaneously in two different parts of the beam. This necessitated placing the Solomon chamber in the beam sufficiently far off the axis so that it did not affect in any way the radiation entering the B. S. chamber. This position was such that it was impossible to see the thimble chamber when sighting back through the B. S. diaphragms.

The X-ray tube was placed in a horizontal oil-filled tank so that the radiation passed through a constant filter of 20 mm of oil + 1.0 mm of aluminum. The tube tank was not sufficiently adjustable to provide a horizontal X-ray beam; and, since the B. S. equipment could not well be used vertically, the beam was brought out at an angle of about 30° with the horizontal. The short optical bench supported by tripods of different heights was inclined at this angle, as sketched in Figure 7. The limiting diaphragm was about 3 cm in diameter.

[23] I. Solomon, J. de Rad. et d'Elec., vol. 8, p. 851; 1924; vol. 10, p. 155; 1926; vol. 11, p. 286; 1927.

The thimble chamber had an effective length of about 3 cm and was placed 44.5 cm from the X-ray tube target and just off the center of the beam entering the B. S. chamber. The front diaphragm of the B. S. chamber was 58.2 cm from the X-ray tube target. As checked later, radiation scattered from the B. S. chamber did not produce a detectable effect on the thimble chamber readings.

Curve III in Figure 4 shows the distribution of intensity across the X-ray beam as obtained by the B. S. chamber. The working positions of both chambers are indicated by the arrows.

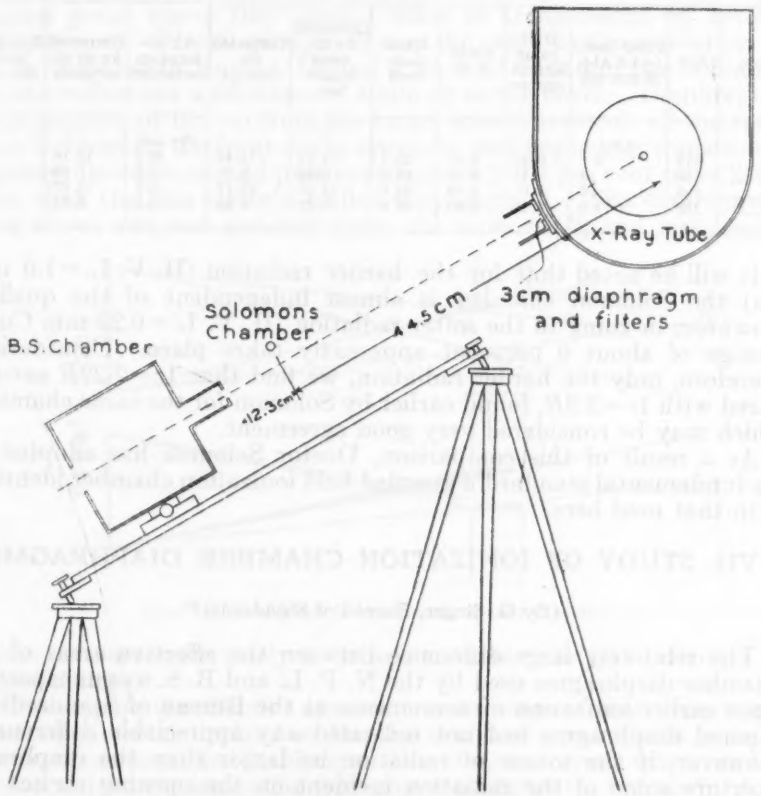

FIGURE 7.—*Diagram of X-ray system in Paris*

Corrections are necessary in this case for the inverse square law and air absorption. The former was applied for the difference in distance of the thimble chamber axis and the front of the B. S. chamber diaphragm from the target. This required that the readings of the thimble chamber be multiplied by a factor of 0.585. The latter was applied for the distance between thimble chamber and the B. S. collector electrode—a distance of approximately 26 cm. Absorption coefficients were taken from available data. However, as a rough check on these corrections they were also obtained experimentally by moving the thimble chamber in a direction along the beam axis. This could not be done with very great accuracy, but the results indicated the corrections used to be valid within the experimental limits.

A further correction for temperature and pressure is necessary in this case because the Solomon unit is defined for room temperature. Since the measurements were made at 19° C. and 762 mm mercury, a factor of 6.97 per cent was applied to the B. S. chamber readings. The average deviation from the mean for all the observations was about ±0.4 per cent.

Table 6 gives the results.

TABLE 6.—*Comparison with Dr. I. Solomon at L'Hopital St. Antoine*

Run	Kv	Filter (mm) (+1.0 Al+ 20 mm oil)	Half-value layer in copper	r/min B. S.	*R*/min Solomon	Corrected for inverse square law	Corrected for leakage	Air absorption correction	Corrected for air absorption	B. S. unit ratio Sol. unit
		Cu.						*Per cent*		
1	110	0	0.25	5.81	22.5	13.15	12.49	0.5	12.18	2.10
2	150	.4	.75	3.47	14.5	8.48	8.06	1.0	7.94	2.28
3	190	.5	1.0	5.85	24.8	14.50	13.77	1.5	13.63	2.29
4	190	1.0	1.5	3.85	16.0	9.37	8.90	2.5	8.85	2.30

It will be noted that for the harder radiation (H. V. L. = 1.0 mm Cu) the Solomon chamber is almost independent of the quality. However, in going to the softer radiation (H. V. L. = 0.25 mm Cu) a change of about 9 per cent apparently takes place. Considering, therefore, only the harder radiation, we find that $1r = 2.29R$ as compared with $1r = 2.2R$, found earlier by Solomon for the same chamber, which may be considered very good agreement.

As a result of this comparison, Doctor Solomon has adopted as his fundamental standard a guarded field ionization chamber identical with that used here.

VII. STUDY OF IONIZATION CHAMBER DIAPHRAGMS

(By G. Singer, Bureau of Standards)[24]

The relatively large difference between the effective areas of the chamber diaphragms used by the N. P. L. and B. S. was unexpected, since earlier ionization measurements at the Bureau of Standards on tapered diaphragms had not indicated any appreciable difference.[25] However, if the source of radiation be larger than the diaphragm aperture some of the radiation incident on the opening strikes the cylindrical wall of the hole in the diaphragm and is effectively cut off as illustrated in Figure 8, *a*. This shifts the effective target-diaphragm position from the outer face toward the inner face of the diaphragm, as well as causing an effective shrinking of the diaphragm opening.

The taper diaphragm (fig. 8, *b*) does not present this difficulty if used far enough from the target to prevent radiation hitting the wall of the aperture. It has the disadvantage, however, of introducing arbitrary factors in the diaphragming system. Furthermore, with steep tapers the front edge of the diaphragm may actually transmit some radiation.

[24] Washington, June 28, 1931.

[25] L. S. Taylor and G. Singer, B. S. Jour. Research, vol. 4 (RP169), p. 631; 1930. In reviewing this work it was found that the experimental conditions were not sufficiently like those described above to warrant comparison.

As a result of the discrepancy between the N. P. L. and B. S. measurements, three carefully constructed diaphragms of the types shown in Figure 5 *A*, *C*, and *D*, were compared at the Bureau of Standards. These were used successively on the ionization chamber at a distance of 100 cm from the target and ionization measurements made for the same X-ray output.

The actual measurements of the diaphragms are given in Table 7. Diaphragms *A* and *C* were both drilled and reamed without taper in lead-bismuth plates 10 mm thick, *C* then being beveled off at the back so as to give a resultant thickness of 4 mm.[26] From the explanation given above they should differ in transmission by roughly 1.2 per cent. The diaphragm *B* was the same as those used on the B. S. chamber in Europe, having a taper of 0.02 mm per millimeter on the radius and a thickness of 4 mm up to the bevel. Diaphragm *B* at a distance of 100 cm from the target should transmit all the radiation incident on the front of the aperture; and neglecting transmission through its edges should pass approximately 0.4 per cent more radiation than the thin straight-walled diaphragm *C*. The diaphragm *D* had about two and one-half times the taper of *B*, and was used in

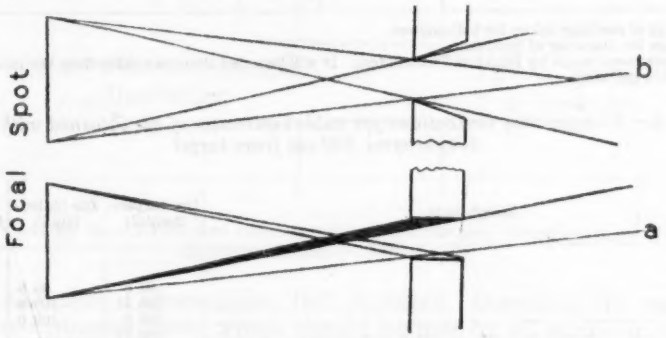

FIGURE 8.—*Effect of thick and tapered diaphragms*

these measurements solely to bring out more clearly the effect of the tapered walls.

To compare the effective areas or transmissions of these diaphragms the volume of air ionized within the chamber is calculated from the measurements of the diaphragm diameter, and from which in turn is determined the ionization per cubic centimeter (I_{cc}) of air.[27] I_{cc} is, of course, directly proportional to the effective diaphragm opening. The results are given in Table 8.

The diaphragm *C* (thin, straight walls) is used as a base in the experimental and calculated values of I_{cc} both being taken as 100. The agreement between the two sets of values is as close as may be expected. It is seen, however, that the difference between *A* and *B* is only 1.7 per cent, whereas, at the N. P. L. the experimentally determined difference between essentially similar diaphragms was apparently 5.4 per cent. A possible cause of this discrepancy may lie in errors in the measurements of the diaphragms as shown below.

The accurate measurement of the diameters of the apertures presented some unexpected difficulties. The B. S. tapered dia-

[26] This type of diaphragm has always been used in previous experiments at the Bureau of Standards.
[27] L. S. Taylor, B. S. Jour. Research, vol. 3 (RP119), p. 807; 1929.

phragms were measured by a method described by Failla [28] wherein an accurately known tapered mandrel was forced into the lead-bismuth diaphragm a given distance. Binks measured two of our diaphragms while at Teddington, with a micrometer microscope, and found diameters of 8.005 and 8.035 mm, respectively, whereas, they were both supposed, from mandrel measurements, to be 8.000 mm.

TABLE 7.—*Diameter measurements of lead-bismuth alloy diaphragms made by Bureau of Standards gage section*

Diaphragm	Microscope			Plug gage	Adopted value
	Front face	Back face	Mean		
	mm	mm	mm	mm	mm
A	8.041	8.037	8.042	8.024	8.033
	8.046	8.043			
B	[1] 7.993	[1] 8.159	[2] 7.993		7.993
C	8.038	8.044	8.038	8.016	8.027
	8.028	8.039			
D	8.032	8.376	[2] 8.040	8.034	8.037
	8.047	8.379			
B (by Binks [3])	8.005	8.170	[2] 8.005		8.005

[1] Average of readings taken for 6 diameters.
[2] Average for diameter of front face.
[3] Measurements made by Binks in Teddington. It will be noted that they differ from our measurements by only 0.15 per cent.

TABLE 8.—*Comparative ionizations per cubic centimeter of air obtained with different diaphragms 100 cm from target*

Diaphragm	I/cc (experimental)	I/cc (calculated)	Observational error
			Per cent
A	98.6	98.8	±0.17
B	100.31	100.4	±.20
C	100.0	100.0	±.17
D	100.79		±.17

To check the reliability of the microscope or other methods the diaphragms *A*, *B*, *C*, *D*, in Figure 5 were measured by the gage section of the Bureau of Standards [29] using both the micrometer-microscope and plug-gage methods. Diaphragm *B* is the same one measured by Binks. The results given in Table 7, show that the micrometer microscope measurements are consistently larger than the plug-gage measurements. An explanation for this discrepancy is at once obvious from an exaggerated cross section of a diaphragm in Figure 9. The microscope method measures only the face diameter of the hole which is likely to be somewhat beveled or worn in the process of making. The plug gage, on the other hand, measures the diametral separation between the highest projecting ridges within the bore. The diameters used in the present study were the average from the two sets of measurements and are estimated by the gage section not to be in error by more than one-tenth per cent.

It should be mentioned that even when using hard lead it was found impossible to make circular holes. Warping tended invariably to

[28] G. Failla, Am. J. Roent. and Ra. Ther., vol. 21, p. 47; 1929.
[29] We are indebted to Drs. L. V. Judson and D. R. Miller, of the Bureau of Standards gage section, for their willing cooperation in this work.

make elliptically shaped openings. As a consequence the bureau is discontinuing the use of lead diaphragms and will in the future use a hard gold or lead-calcium alloy wherein the surface can be accurately lapped and be relied upon to hold its dimensions.

VIII. CONCLUSION—JOINT RECOMMENDATIONS OF THE BUREAU OF STANDARDS, NATIONAL PHYSICAL LABORATORY, PHYSIKALISCH-TECHNISCHE REICHSANSTALT, AND LE SERVICE D'ETALONNAGE DE L'HOPITAL ST. ANTOINE

Table 9 is given to summarize the results of all of the comparisons. The size of roentgen as measured by each laboratory is referred to that measured by the B. S. chamber as a base.

Thus the agreement between the National Laboratories is as close as may be reasonably expected and much better than necessary to-day for practical calibration purposes.

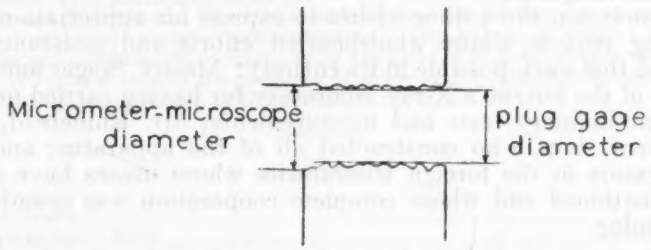

FIGURE 9.—*Magnified cross section of diaphragm showing where diameter measurements apply*

The National Laboratories feel justified, therefore, in making certain recommendations which should be met by all open-air ionization chambers in order to avoid gross errors. It is believed that these are neither restrictive nor unduly arbitrary. These are:

1. The use of an X-ray tube having a focal spot as small as possible (up to 8 mm diameter).

2. The use of a diaphragm placed as close to the tube as possible and having an aperture of such size as to shield from the ionization chamber all radiation except that from the face of the target.

TABLE 9.—*Summary of comparisons made between the Bureau of Standards and foreign laboratories*

Laboratory	Tube voltage (kv)	H. V. L. (mm copper)	Size of unit (number of units per B. S. unit)	Error in comparisons
				Per cent
B. S. large chamber	100–170	0.1 –1.1	1.0005	±0.25
N. P. L.[1]	110–140	.11– .5	1.001	±.9
N. P. L.[2]	110–140	.11	.9886	±.9
N. P. L.[3]	110–140	.11– .5	.996	±.9
P. T. R	100–180	.16–1.1	1.0035	±.4
Solomon	110	.25	2.10	±.4
	150–190	.75–1.5	2.29	±.4

[1] Corrections made for diaphragm differences.
[2] Same diaphragm used on both chambers.
[3] Averaging all readings taken.

3. The use of a standard chamber diaphragm having a minimum thickness, but such that not more than one-tenth of the radiation measured passes through the material of the diaphragm.

4. The use of a standard ionization chamber aperture of about the same diameter as the focal spot; however, not to be much smaller.

5. The utilization of only that portion of the X-ray beam in which the intensity within the experimental limits is uniform.

6. The use of the shortest distance between chamber diaphragm and collector electrode.

7. The use of a current-measuring method wherein the potential difference between the guards and collector plate is negligible; preferably a null method.

Doctor Solomon has announced [30] his acceptance of the open-air ionization chamber as his fundamental standard while at the same time recognizing the secondary calibration with radium as heretofore used by him. For this purpose he will employ an exact duplicate of the Bureau of Standards guarded field ionization chamber as used in this investigation.

In conclusion the author wishes to express his appreciation to the following persons whose wholehearted efforts and assistance have rendered this work possible in its entirety: Messrs. Singer and Stoneburner, of the bureau's X-ray laboratory for having carried out most of the preliminary tests and measurements; Mr. Rhinebold, of our instrument shop, who constructed all of the apparatus; and those investigators in the foreign laboratories whose names have already been mentioned and whose complete cooperation was essential and forthcoming.

WASHINGTON, October 1, 1931.

[30] Proceedings of Committee on X-Ray Units of Third International Congress of Radiology (unpublished).

RP 398

VOLUMETRIC DETERMINATION OF PENTOSES AND PENTOSANS [1]

By G. M. Kline and S. F. Acree

ABSTRACT

The determination of pentoses and pentosans involves two steps, namely, distillation of the sample with 12 per cent hydrochloric acid and estimation of the furfural in the distillate. It was found that steam distillation did not give any better yields of furfural from xylose than the standard method of distillation. Gravimetric and volumetric procedures for determining the distilled furfural were studied with particular reference to the excess bromine titration method of Powell and Whittaker. The latter method has the advantages of speed and accuracy over wide ranges of concentration. The effects of various chemical substances and experimental conditions on the yield of furfural were investigated. The loss of furfural due to the presence of nitric acid in the distillation mixture was reduced by precipitation of the nitrates with nitron.

CONTENTS

	Page
I. Introduction	25
II. Experimental work	27
1. Effect of distillation method on furfural yield	27
2. Relative accuracy of gravimetric and volumetric methods for determining furfural	29
3. Rate of distillation of furfural from a xylose-hydrochloric acid mixture by steam	32
4. Effect of various chemical substances on the yield of furfural	32
5. Effect of exposure to air on loss of furfural	34
6. Effect of washing furfuralmalonylthiourea precipitate with water and hydrochloric acid	34
III. Discussion of results	35
IV. Summary and conclusions	35

I. INTRODUCTION

The "standard" method for the determination of pentosans is distillation of the sample with 12 per cent hydrochloric acid and precipitation of the resultant furfural with phloroglucinol.[2] This method has many disadvantages: (1) It is empirical; (2) experimental conditions, such as concentration of carbohydrate and acid, and rate of distillation must be carefully controlled; (3) it is time-consuming; (4) an artificial set of corrections must be applied; and (5) it is lacking in accuracy.

Considerable investigation has been devoted in recent years to finding a better method, particularly with regard to the estimation of

Read in part at the Buffalo meeting of the American Chemical Society, September, 1931.

[1] Acknowledgement is made of the contributions of W. L. Hall, G. W. Irving, W. Seaton, C. S. Slater, and B. Wingfield to the studies described in this paper.

[2] Official and Tentative Methods, Association of Official Agricultural Chemists, p. 120; 1925.

the distilled furfural. The procedure that seems to have met with the most favor is the thiobarbituric acid method of Dox and Plaisance.[3] This method, however, like that employing phloroglucinol, is a precipitation procedure and has many of the disadvantages of the "standard" method. Sweeney [4] concludes that "from the standpoint of difficulties encountered in the manipulation of the determinations the methods are about equal." It will be shown in this paper that the use of thiobarbituric acid has the disadvantage that very small quantities of furfural can not be determined accurately. The phloroglucinol method also becomes less accurate for small amounts of furfural.

Several volumetric methods have been proposed for the determination of furfural distilled from pentosans. Pervier and Gortner [5] have published a review of the earlier proposals. These authors also describe a method involving the titration of furfural in acidified potassium bromide solution with potassium bromate. The reagent is added slowly from a burette until free bromine persists in the solution as indicated electrometrically. Under these conditions 1 molecule of bromine reacts with 1 molecule of furfural. However, there is a tendency for the oxidation product to react further with bromine, and subsequent workers have found great difficulty in determining the end point by the above procedure.

The use of an excess of bromine to react with the furfural and titration of the unused bromine has been proposed by Van Eck [6] and Powell and Whittaker.[7] This method, as described by the latter authors, has the advantage that the analysis can be completed in a single day instead of the two to three days required by the precipitation methods. In fact, after the distillation of the furfural is completed, the analysis can be finished in a little more than an hour by the volumetric procedure, whereas the precipitation methods require that the precipitate be allowed to stand overnight before filtering, and further that the precipitate be dried at 105° for from four hours to overnight before weighing. Powell and Whittaker have found very good agreement in the results of pentosan determinations made on wood cellulose by their bromine method and the standard phloroglucinol method. Schorger [8] has included a description of this method in his book, "The Chemistry of Cellulose and Wood." Three recent articles [9] have appeared in foreign journals recommending the use of this method or modifications of it, but no study or application of it has been published in this country.

The standard method [10] for distillation of samples containing pentoses or pentosans prescribes the addition of 100 ml of 12 per cent hydrochloric acid to the material in a 250 ml flask and distillation at the rate of 30 ml in 10 minutes. As soon as 30 ml of distillate are collected, a like amount of the 12 per cent hydrochloric acid is added

[3] Dox, A. W., and Plaisance, G. P. J. Am. Chem. Soc., vol. 38, p. 2156; 1916. Wise, L. E., and Peterson, F. C. Ind. Eng. Chem., vol. 22, p. 362; 1930. Hansen, L. P., Paper presented before the sugar division at the Cincinnati meeting of the American Chemical Society; September, 1930.

[4] Sweeney, O. R. Bulletin 73, Iowa Engineering Experiment Station.

[5] Pervier, N. C., and Gortner, R. A., Ind. Eng. Chem., vol. 15, p. 1255; 1923.

[6] Van Eck, P. N., Versl. v. d. Verricht. v. h. centr. lab. v. d. Volksgezondh.; 1918. Chem. Abstr., vol. 14, p. 509; 1920.

[7] Powell, W. J. and Whittaker, H., J. Soc. Chem. Ind., vol. 43, p. 35T; 1924.

[8] Schorger, A. W., The Chemistry of Cellulose and Wood; 1926.

[9] Kullgren, C., and Tyden, H., Ing. Vetenskaps Akad. Handl.; 1929, No. 94, pp. 3–62. Chem. Abstr., vol. 24, p. 1316; 1930. Deshpande, D. D., J. Indian Inst. Sci., vol. 13A, p. 110; 1930. Sasaki, K., J. Agr. Chem. Soc. Japan, vol. 6, p. 538; 1930, Chem. Abstr., vol. 24, p. 5670; 1930.

[10] See footnote 2, p. 25.

to the flask through a separatory funnel; the distillation is continued in this manner until 360 ml of distillate are collected. This procedure has been criticized on the grounds that the furfural is decomposed by the concentrated hydrochloric acid vapors. The use of steam distillation has been suggested by Jolles [11] and Pervier and Gortner, and practically quantitative results reported. The avoidance of destruction of furfural has been assumed to be due to the low acidity of the distillate and to the prompt removal of the furfural by the current of steam.

This paper presents the results of a study of the standard and steam distillation procedures, a comparison of volumetric bromine methods and the gravimetric thiobarbituric acid method for determining furfural, and the effect of various conditions and substances on the yield of furfural.

II. EXPERIMENTAL WORK

1. EFFECT OF DISTILLATION METHOD ON FURFURAL YIELD

In order to determine the relative efficiency of the standard and steam distillation methods similar aliquots of a solution of xylose were distilled by the two procedures.

(a) STANDARD METHOD OF DISTILLATION

The method of the Association of Official Agricultural Chemists was used. The sample is placed in a 250 ml flask and 100 ml of 12 per cent hydrochloric acid (specific gravity 1.06) are added. Distillation is conducted at the rate of 30 ml in 10 minutes. The distillate is passed into the receiver through a small filter. As soon as 30 ml of distillate are collected, 30 ml of 12 per cent hydrochloric acid are added to the flask. Distillation is continued in this manner until 360 ml of solution have been collected.

(b) STEAM DISTILLATION METHOD

The steam distillation method was used as proposed by Pervier and Gortner except that the temperature of distillation rose to about 108° instead of the 103° to 105° recommended by these authors. They found, however, that theoretical results were also obtained by steam distillation at temperatures of 107° to 108°. The weighed sample and 200 ml of 12 per cent hydrochloric acid are placed in a 750 ml flask fitted up for steam distillation. A slow current of steam is conducted into the mixture and as soon as the boiling temperature is reached, the distilling flask is heated with a low flame. Distillation is continued until the distillate no longer gives a red coloration with aniline acetate test paper.

The distillation of 0.0697 g of xylose by each of these methods yielded practically equal amounts of furfural. Table 1 shows that the percentage of xylose recovered as furfural was not the theoretical value, but only about 88 to 92 per cent of the total. These two experiments indicate that the destruction or loss of furfural is not avoided by using steam distillation.

Further evidence that the standard and steam distillation methods give about the same yield of furfural is afforded by the data presented in Table 2. The distillation of 0.03 to 0.5 g xylose gives an amount

[11] Jolles, A., Sitz. Akad. Wiss. Wien, vol. 114, Abt. II, p. 1191; 1905.

of furfural equivalent to 73 to 88 per cent of the xylose as determined by precipitation of the furfural with thiobarbituric acid. Similar results were obtained by two different investigators in this laboratory. These values are more nearly in agreement with the yields of xylose resulting from distillation according to the standard procedure and precipitation with phloroglucinol as found by Krober than with the theoretical yields reported by Pervier and Gortner. It would appear, therefore, that steam distillation does not materially improve the yield, and that further work is needed upon this problem of obtaining theoretical yields of furfural from xylose.

TABLE 1.—*Comparison of the "standard" and steam distillation methods for converting xylose to furfural*

Weight of xylose	Method of distillation	Yield of furfural		Xylose recovered	
		Thiobarbituric acid method	Excess bromine method	Thiobarbituric acid method	Excess bromine method
g		*g*	*g*	*Per cent*	*Per cent*
0.0697	Standard	0.0392	0.0412	88.02	92.35
.0697	Steam	.0392	.0410	88.02	91.93

TABLE 2.—*Estimation of xylose by gravimetric and volumetric determination of the distilled furfural*

[Samples of pure xylose were steam distilled with 12 per cent hydrochloric acid. The distillate was made up to 500 ml and 200 ml aliquots taken for each determination. Data are expressed as total recovery]

Weight of xylose	Xylose found	
	Precipitation with thiobarbituric acid	Bromine titration
g	*Per cent*	*Per cent*
[1] 0.0127	51.63	
.0139	29.10	93.53
½ .0346	73.00	
½ .0662	74.15	
.0697	88.02	91.93
.1393	83.05	85.06
½ .1673	83.60	
.2786	83.29	81.52
½ .3376	83.40	
½ .5060	81.85	

[1] These experiments were performed by Baker Wingfield.

TABLE 3.—*Recovery of furfural by distillation*

Weight of furfural	Method of distillation	Method of analysis of distillate	Amount of furfural recovered	Furfural recovered
g			*g*	*Per cent*
[1] 0.1200	Steam	Electrometric-bromate titration	0.1195	99.58
½ .1200	do	do	.1195	99.58
½ .1200	do	do	.1154	96.17
[2] ½ .1062	Standard	Thiobarbituric-acid precipitation	.1054	99.25
[2] ½ .1062	do	do	.1048	98.68

[1] These experiments were performed by C. S. Slater.
[2] These samples were added to the residual liquors from the distillation of 3 g portions of peanut shells with 12 per cent hydrochloric acid. The experiments were performed by W. L. Hall.

The data in Table 3 indicate that furfural itself can be recovered with slight losses by distillation with 12 per cent hydrochloric acid either by the standard procedure or with steam. Two of the distillations were carried out in the presence of other organic substances, such as lignin and cellulose present in peanut hulls. The failure to recover an amount of furfural equivalent to the pentoses or pentosans present is, therefore, not due to a destructive action of concentrated hydrochloric acid on furfural, but rather to another reaction of the pentose material during conversion into furfural.

2. RELATIVE ACCURACY OF GRAVIMETRIC AND VOLUMETRIC METHODS FOR DETERMINING FURFURAL

In the course of analysis of extracts of wheat straw, cottonseed hull bran, and samples of xylose, data were obtained on the yields of furfural as indicated by the thiobarbituric acid method and the bromine titration methods of Pervier and Gortner and of Powell and Whittaker on duplicate aliquots of various distillates. The data are given in Table 4.

TABLE 4.—*Comparison of the thiobarbituric acid and bromine methods for the determination of furfural*

[Samples of straw extracts, cottonseed hull bran and xylose were steam distilled with 12 per cent HCl. The distillate was made up to 500 ml and 200 ml aliquots were taken for each determination. Data for xylose are given as the amount of furfural theoretically present and actually recovered in the aliquot analyzed]

Sample	Furfural recovered		
	Thiobarbituric-acid method	Excess-bromine method	Electrometric-bromate titration method
	g	*g*	
1. Straw extract	0. 0000	0. 0019	
2. Xylose=0.0036 g furfural	. 0010	. 0033	
3. Straw extract	. 0000	. 0037	
4. Straw extract	. 0060	. 0075	
5. Straw extract	. 0074	. 0097	
6. Straw extract	. 0133	. 0146	
7. Xylose=0.0178 g furfural	. 0157	. 0164	
8. Straw extract	. 0196	. 0194	
9. Straw extract	. 0241	. 0245	
10. Xylose=0.0357 g furfural	. 0296	. 0303	
11. Xylose=0.0713 g furfural	. 0594	. 0581	
12. Cottonseed-hull bran extract	[1] 0573		[2] 0. 0557
13. Furfural: 1173 g	[1] 1169		[2] 1178

[1] These determinations were made by W. L. Hall.
[2] These determinations were made by C. S. Slater.

(a) THIOBARBITURIC-ACID METHOD

The procedure used was that of Dox and Plaisance described in Sweeney's bulletin on The Commercial Utilization of Corncobs. Exactly 0.9 g of thiobarbituric acid is ground in an agate mortar with just enough water to moisten it. The ground paste is washed into a beaker and made up to 150 ml. After the acid has gone into solution, 75 ml of hydrochloric acid, specific gravity 1.06, are added slowly, with stirring. The solution is filtered through asbestos and is ready for use. For the precipitation, the solution (aliquot) of furfural is made up to 12 per cent hydrochloric acid and treated with twice the theoretical amount of the fresh thiobarbituric acid. The precipitate

which forms is allowed to stand for 24 hours. It is then filtered through a Gooch crucible, washed and dried overnight at 100° C. One gram of the condensation product contains 0.4323 g furfural.

(b) ELECTROMETRIC BROMATE TITRATION METHOD

The proposed method of Pervier and Gortner was followed. To the solution containing furfural 5 ml of 20 per cent potassium bromide are added for every 100 ml of solution and the acidity (HCl) is adjusted to about 4 per cent by weight. With continual stirring $N/10$ potassium bromate solution is run in slowly from a burette until the pale yellow color of bromine persists for a short period. At this point the bromate is added in small increments and the time is recorded which is required for the disappearance of free bromine as indicated by the use of a sensitive galvanometric set-up. As the end point is crossed a rather large increase in the time required will be noted. The number of milliliters of $N/10$ potassium bromate required multiplied by 0.004803 gives the number of grams of furfural in the sample. In this titration 1 molecule of bromine reacts with 1 molecule of furfural.

(c) EXCESS BROMINE METHOD

The procedure recommended by Powell and Whittaker was followed. To make up the standard bromide-bromate solution dissolve 3 g of potassium bromate and 50 g of potassium bromide in distilled water and dilute to 1 liter. The distillate of furfural is made up to 500 ml with 12 per cent hydrochloric acid. Then 25 ml portions of the bromate-bromide reagent are pipetted into glass-stoppered flasks and 200 ml aliquots of the distillate are added to each flask. Also 200 ml of the 12 per cent hydrochloric acid are added to one of the flasks, containing 25 ml of the reagent to serve as a blank. The bottles are allowed to stand in the dark for one hour, and after the addition of 10 ml of 10 per cent potassium iodide solution, the liberated iodine is determined by titration with $N/10$ sodium thiosulphate. The number of milliliters of $N/10$ thiosulphate required by the sample is subtracted from the number of milliliters required by the blank, the difference being a measure of the furfural present. One milliliter of $N/10$ sodium thiosulphate is equivalent to 0.0024 g of furfural. In this method 2 molecules of bromine react with 1 molecule of furfural.

The data in Table 4 show that for amounts of furfural less than 0.01 g the precipitation method gives low results. For very small amounts of furfural, 0.002 to 0.003 g, such as may be obtained from wood cellulose, dilute extracts of raw-plant substances, and materials containing small quantities of pentoses and pentosans as impurities, the precipitation method either fails to indicate the presence of any furfural or precipitates only a small fraction thereof. The excess bromine titration method, however, is sensitive to these small amounts of furfural. Finally the electrometric bromate titration method of Pervier and Gortner gave values in experiments in Tables 3 and 4 with amounts of furfural between 0.05 and 0.12 g which were comparable with the results of analysis with thiobarbituric acid. The data in Table 5 and experiments 3 and 4, Table 6, show, however, that accurate results with small quantities are difficult to obtain with this method. The end point is indefinite due to a second reaction involving the combination of another molecule of bromine with furfural. The method of Powell and Whittaker in which an excess of bromine

is allowed to react with the furfural gives a satisfactory end point. In view of the advantageous combination of speed and accuracy in the excess bromine titration method for determining furfural distilled from pentoses and pentosans as indicated by the published work of Powell and Whittaker, Deshpande and Sasaki, and by the data presented in this paper, it is believed to be worthy of consideration as an official method.

TABLE 5.—*Determination of furfural by electrometric bromate titration* [1]

Weight of furfural taken	Volume of $NaBrO_3$ consumed	Weight of furfural found
g	*ml*	*g*
0.060	12.20	0.0591
.060	12.49	.0605
.060	12.50	.0605
.060	12.60	.0610
.060	12.65	.0612
.060	12.80	.0620
.067	13.45	.0651
.078	15.80	.0765
.1173	24.34	.1178

[1] The experimental data presented in this table were obtained by C. S. Slater.

TABLE 6.—*Rate of distillation of furfural from a xylose-hydrochloric acid mixture by steam*

Experiment No.	Weight of xylose taken	Sample	Weight of furfural found	Weight of xylose found
	g		*g*	*g*
1[1]	0.0697	First 50 ml	0.0057	0.0089
		Second 50 ml	.0085	.0133
		Third 50 ml	.0089	.0140
		Fourth 50 ml	.0093	.0146
		Fifth 50 ml	.0061	.0095
		Sixth 50 ml	.0027	.0042
		Seventh 50 ml.[3]	.0009	.0014
		Eighth 50 ml.[3]	.0005	.0007
		Total	.0426	.0666
2[1]	.0697	400 ml	.0410	.0641
3[2]	.1500	First 50 ml	.0336	.0525
		Second 50 ml	.0305	.0477
		Third 50 ml	.0121	.0189
		Fourth 50 ml	.0068	.0106
		Fifth 50 ml	.0019	.0030
		Sixth 50 ml	.0010	.0016
		Total	.0859	.1343
4[2]	.1500	300 ml	.0905	.1414

[1] The determination of furfural in these experiments was made by the excess-bromine method. In experiment 2 the titration was carried out with a 2/5 aliquot.
[2] The determination of furfural in these experiments was made by C. S. Slater using the electrometric-bromate titration method.
[3] 50 ml of 12 per cent hydrocloric acid were added to the mixture in the distilling flask after 300 and 350 ml, respectively, of distillate had been collected.

Titration of the furfural with iodine and alkali according to the method recently recommended for aldehydic sugars [12] was also attempted. The furfural, however, reacted more slowly with these reagents than did the sugars, and therefore most of the iodine was converted to iodate rather than consumed in the oxidation of the furfural. Higher temperatures and longer time periods did not materially affect the results obtained. These observations confirm the

[12] Kline, G. M., and Acree, S. F., Analytical ed., Ind. and Eng. Chem., vol. 2, p. 413; 1930. B. S. Jour. Research, vol. 5, p. 1063; 1930.

negative results obtained by Pervier and Gortner with sodium hypoiodite.

3. RATE OF DISTILLATION OF FURFURAL FROM A XYLOSE-HYDROCHLORIC ACID MIXTURE BY STEAM

The official method of distillation is assumed to give all of the potential furfural in 360 ml distillate. Using steam distillation Pervier and Gortner collected an average of 800 ml; moreover, with 0.2 g samples of xylose volumes of distillate varying from 300 to 1,000 ml apparently gave quantitative recoveries of the sugar as furfural. Experiments on the rate of distillation of furfural are presented in Table 6. The amount of furfural distilling over fell off rapidly after 200 ml had been collected. The amount of furfural present in any 50 ml portion in experiment 1 was less than 0.01 g. In view of the results of the experiments in Table 4, it is readily seen that the precipitation method would not have been practical for estimating such small amounts of furfural. Therefore, with a more sensitive method, such as was used in these experiments for determining furfural, it may be found that the usual practice of collecting 360 ml of distillate does not obtain all the furfural that it is possible to distill from the pentoses or pentosans.

4. EFFECT OF VARIOUS CHEMICAL SUBSTANCES ON THE YIELD OF FURFURAL

It has been noted in a previous article [13] that the presence of nitric acid results in a lowered yield of furfural. These conditions are encountered particularly in extracts made with nitric acid or in nitrated materials. Table 7 shows the effect of increasing amounts of nitrates on the yield of furfural. In the presence of large amounts of nitrates (1.5 g KNO_3) the effect of the hydrochloric-nitric acid mixture is such that no furfural at all is found in the distillate. The nitric acid may act directly on the xylose as discussed in another article,[14] or it may oxidize the furfural. The last two experiments in Table 7 indicate that the nitric acid or possibly chlorine acts upon the furfural rather than on the pentose or pentosan.

To overcome this action of nitric acid the effect of the addition of various reducing agents to xylose and xylose-nitrate mixtures was studied. The results are presented in Table 8. Stannous chloride in 5 g amounts caused lower yields of furfural than the 0.1675 g KNO_3. Sulphurous acid, ferrous sulphate, and ferrous ammonium sulphate did not materially affect the yield of furfural from xylose, but they also had very little effect in decreasing the loss of furfural due to action of the nitric acid. The addition of small amounts of hydrazine sulphate and urea to xylose-nitrate-ferrous ammonium sulphate mixtures resulted in smaller yields of furfural. Removal of the nitrates by precipitation with nitron and filtration gave much better yields of furfural. Nitron itself had only a slight effect on the yield of furfural from xylose alone. It is therefore recommended that in determining the pentosan content of nitrate-containing materials preliminary treatment with nitron be carried out before liberating furfural.

---

[13] Hall, W. L., Slater, C. S., and Acree, S. F., B. S. Jour. Research, vol. 4, p. 329; 1930.
[14] Kline, G. M., and Acree, S. F., Ind. & Eng. Chem., vol. 22, p. 975; 1930.

TABLE 7.—*Effect of varying amounts of nitrates on furfural yield* [1]

[All samples made up to 100 ml volume and 12 per cent HCl and distilled by standard procedure. Furfural determined by thiobarbituric acid precipitation method]

No. of experiment	Sample	Weight thiobarbituric acid precipitate	Equivalent weight of furfural	Equivalent weight of xylose	Xylose recovered	Xylose found using Krober's table
		g	*g*	*g*	*Per cent*	*Per cent*
I 1	0.2003 g xylose	0.2570	0.1111	0.1736	86.69	97.65
I 2	do	.2590	.1120	.1750	87.37	98.50
I 3	0.2003 g xylose+0.0125 g KNO_3	.2484	.1073	.1678	83.79	94.26
I 4	do	.2540	.1098	.1716	85.68	96.51
I 5	0.2003 g xylose+0.0250 g KNO_3	.2470	.1068	.1669	83.32	93.81
I 6	do	.2467	.1067	.1667	83.22	93.76
S 7	0.2003 g xylose+0.0300 g KNO_3	.2501	.1081	.1690	84.36	95.01
I 8	0.2003 g xylose+0.0500 g KNO_3	.2242	.0969	.1515	75.63	85.17
I 9	do	.2280	.0986	.1540	76.91	86.67
S 10	0.2003 g xylose+0.0625 g KNO_3	.2154	.0931	.1455	72.66	81.83
I 11	0.2003 g xylose+0.0875 g KNO_3	.1860	.0804	.1257	62.74	70.74
I 12	do	.1936	.0837	.1308	65.31	73.59
I 13	0.2003 g xylose+0.1250 g KNO_3	.1751	.0757	.1183	59.07	66.55
I 14	do	.1773	.0767	.1198	59.81	67.45
I 15	0.2003 g xylose+0.1675 g KNO_3	.1510	.0653	.1020	50.94	57.46
S 16	do	.1536	.0664	.1038	51.81	58.46
S 17	0.2003 g xylose+1.5000 g KNO_3	None.				
H 18	0.1173 g furfural+0.1250 g KNO_3	.1738	.0751		[2] 64.05	
H 19	do	.1732	.0749		[2] 63.83	

[1] The experiments in this table were performed by W. L. Hall, G. W. Irving, and W. Seaton.
[2] Per cent furfural recovered.

TABLE 8.—*Effect of various substances on the loss of furfural due to nitrates* [1]

All samples made up to 100 ml volume and 12 per cent HCl concentration, and distilled by standard procedure. Furfural determined by thiobarbituric acid precipitation method]

No. of experiment	Sample	Weight thiobarbituric acid precipitate	Equivalent weight of furfural	Equivalent weight of xylose	Xylose recovered	Xylose found using Krober's table
		g	*g*	*g*	*Per cent*	*Per cent*
S 1	0.2003 g xylose+0.1675 g KNO_3+5 g $SnCl_2 \cdot 2H_2O$.	0.1431	0.0619	0.0967	48.27	54.47
S 2	0.2003 g xylose+5 g $SnCl_2 \cdot 2H_2O$	.1372	.0593	.0927	46.28	52.22
S 3	0.2003 g xylose+0.1250 g KNO_3+1.5 g H_2SO_3	.1812	.0783	.1224	61.12	68.85
S 4	0.2003 g xylose+1.5 g H_2SO_3	.2627	.1136	.1775	88.61	99.85
S 5	0.2003 g xylose+0.1675 g KNO_3+25 g $FeSO_4 \cdot 7H_2O$.	.1861	.0805	.1257	62.78	70.84
S 6	0.2003 g xylose+25 g $FeSO_4 \cdot 7H_2O$	.2482	.1073	.1677	83.72	94.26
S 7	0.2003 g xylose+0.1675 g KNO_3+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$.	.2145	.0927	.1449	72.36	81.48
I 8	0.2003 g xylose+0.1675 g KNO_3+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$.[2]	.1634	.0706	.1104	55.12	62.11
I 9	0.2003 g xylose+0.1675 g KNO_3+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$.[2]	.1447	.0626	.0978	48.81	55.17
S 10	0.2003 g xylose+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$.	.2584	.1117	.1746	87.16	98.20
I 11	0.2003 g xylose+0.1675 g KNO_3+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$+0.5 g hydrazine sulphate.	.1959	.0847	.1324	66.08	74.49
I 12	0.2003 g xylose+0.1675 g KNO_3+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$+0.25 g urea.	.2033	.0879	.1374	68.58	77.28
I 13	0.2003 g xylose+0.1675 g KNO_3+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$+0.50 g urea.	.1825	.0789	.1233	61.56	69.40
I 14	0.2003 g xylose+0.1675 g KNO_3+10 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$+1.0 g urea.	.1715	.0741	.1159	57.85	65.20
I 15	0.2003 g xylose+0.1250 g KNO_3+1 g nitron [2] [3]	.2336	.1010	.1578	78.80	88.77
I 16	0.2003 g xylose+0.1250 g KNO_3+1 g nitron [2] [3].	.2160	.0934	.1459	72.86	82.13
I 17	0.2003 g xylose+0.5 g nitron	.2565	.1109	.1733	86.52	97.45
I 18	0.2003 g xylose+0.5 g nitron	.2579	.1115	.1742	86.99	98.00

[1] The experiments in this table were performed by G. W. Irving and W. Seaton.
[2] Solution filtered before making up to 12 per cent HCl and distilling.
[3] Precipitate of nitron-nitrate equivalent to 0.1234 g out of 0.1250 g KNO_3.

TABLE 9.—*Loss of furfural on exposure to air* [1]

Sample	Time exposed	Amount furfural originally present	Volume of $NaBrO_3$ consumed	Amount furfural found
		g	*ml*	*g*
10 ml 0.6 per cent furfural solution, 10 ml 8 per cent HCl and 1 ml 20 per cent KBr	40 minutes	0.060	10.30	0.0499
10 ml 0.6 per cent furfural solution, 10 ml 8 per cent HCl	50 minutes	.060	10.25	.0496
10 ml 0.6 per cent furfural solution	65 minutes	.060	8.5	.0411
	16 hours	.060	0.5	.0024
	do	.060	0.4	.0019

[1] These experiments were performed by C. S. Slater.

5. EFFECT OF EXPOSURE TO AIR ON LOSS OF FURFURAL

In a few experiments in which several samples of furfural solutions were prepared at one time and analyzed in succession by the electrometric bromate titration method, a decreasing yield of furfural was noted. Inasmuch as the flasks had been open to the air, loss due to volatilization of furfural was suspected. A series of experiments in which the furfural solutions were left exposed to the air for varying lengths of time before analysis is presented in Table 9. These experiments show that after 16 hours very little furfural remains in the solution. It would seem that some protection of the distillate from exposure to air during the two hours required for completion of the distillation would be advisable. The filtration device used by us in the mouth of the graduate cylinder receiving the distillate was a folded filter inside a funnel with a cover of paper or glass containing a hole through which the condenser passed. This arrangement probably prevents evaporation to a large extent by protecting the distillate from air currents inasmuch as the yields of furfural from pure solutions of furfural are nearly quantitative. However, in the present standard apparatus, the distillate is largely unprotected from the time it reaches the end of the condenser open to the air until it passes through the filter paper.

6. EFFECT OF WASHING FURFURALMALONYLTHIOUREA PRECIPITATE WITH WATER AND HYDROCHLORIC ACID [15]

In the experimental determination of furfural by precipitation with thiobarbituric acid, it was found that when the filtered precipitate is excessively washed with distilled water a cloudiness appears stratified upon the first filtrate. This cloudiness was found also, though to a lesser degree, when washings were made with 3 and 6 per cent hydrochloric acid. Washing with 12 per cent hydrochloric acid gave no cloudiness. However, washings with 12 per cent hydrochloric acid on standing showed a slight sediment in the bottom of the flask. This sediment was also found when the precipitating reagent (acidified thiobarbituric acid) was made up to the same concentration of hydrochloric acid as would be found in the filtrate. The sediment in the second case is therefore not the furfuralmalonylthiourea, but comes from the thiobarbituric acid. Washing a weighted amount of the dried furfural precipitate with water and hydrochloric acid showed slight losses for both, but in this experiment the precipitates are not in the same physical condition as those obtained in carrying

[15] This experimental work on washing the precipitate was performed by W. L. Hall.

out the analysis. If some of the furfuralmalonylthiourea is shaken up in water and allowed to become saturated overnight and then filtered, the filtrate is slightly cloudy. Colloidal particles can be seen with the ultramicroscope. Addition of 12 per cent hydrochloric acid to the filtrate causes the colloidal particles to settle out. From this it seems evident that washing the fresh precipitate with water causes the formation of a colloidal solution whereas the use of 12 per cent hydrochloric acid prevents it. It is therefore recommended that the excess thiobarbituric acid reagent be removed from the precipitate by washing with 12 per cent hydrochloric acid rather than with water.

III. DISCUSSION OF RESULTS

A number of workers have tried the method of Pervier and Gortner with its indefinite end point, and, finding it tedious and difficult to obtain consistent results, have abandoned the bromine method altogether. Our studies have shown that by using an excess of bromine to react with the furfural and determining the bromine left by the use of potassium iodide and thiosulphate solutions we can make the furfural determination quickly and accurately. Although the method has been said to have the disadvantage that no corrections can be applied for hydroxymethyl-furfural, methylfurfural, and oxidizable impurities that may be obtained in appreciable quantities from raw plant substances, the results obtained for wood pulp and purified wood by Powell and Whittaker and for straw extracts by our experiments show good agreement between the volumetric and precipitation procedures. The great saving, both in personal attention required and in the time elapsing before the results can be reported should stimulate a further study of this volumetric procedure.

IV. SUMMARY AND CONCLUSIONS

The results of a study of the standard and steam distillation procedures for the formation and separation of furfural from xylose, a comparison of the volumetric bromine methods and the gravimetric thiobarbituric acid method for determining furfural, and the effect of various chemical substances and experimental conditions on the yield of furfural are presented in this paper.

Steam distillation did not give any better yields of furfural from xylose than the standard method of distillation.

The excess bromine titration method for determining furfural distilled from pentoses and pentosans has the advantages of speed and accuracy over wide ranges of concentration. It is suggested that this method is worthy of consideration as an official method.

The presence of nitric acid or nitrates in the distillation mixture causes the destruction of furfural. This loss can be greatly reduced by preliminary removal of the nitrates with nitron.

It is felt that the phase of this subject needing most attention at this time is the study of the best conditions for the conversion of the pentose or pentosan into practically 100 per cent of furfural. The yields are too low and variable at present.

WASHINGTON, June 30, 1931.

A METHOD FOR DETERMINING THE VOLUME CHANGES OCCURRING IN METALS DURING CASTING

By C. M. Saeger, jr., and E. J. Ash [1]

ABSTRACT

This paper reviews methods which have been proposed and used for determining the various types of shrinkage undergone by a cooling metal. The three types of shrinkage to be considered may be defined as (*a*) shrinkage in the liquid metal, (*b*) shrinkage during solidification, and (*c*) shrinkage in the solid state. It also considers briefly the sand-cast cone method for determining total shrinkage during casting and the more fundamental procedure of constructing a specific volume-temperature curve for each metal or alloy from some temperature well above the melting point or melting range to room temperature. The specific volume-temperature curve in the range of liquid metal is constructed from data secured by application of the crucible-immersion method; that is, by filling a crucible of known volume with liquid metal at known temperature. Since the mass of the sample of liquid metal is the same as that of the sample at room temperature, the specific volume of the liquid can be readily calculated. Data on the contraction of the solid metal were obtained by direct observations of the change in length with change in temperature of a sand-cast bar of metal. The difference between the specific volume of the solid metal and of the liquid metal at the melting point is the shrinkage during solidification. In the case of an alloy, shrinkage during solidification occurs over a range of temperature.

CONTENTS

	Page
I. Introduction	37
1. Importance of problem	37
2. Definitions and general aspects of shrinkage	38
II. Previous methods	39
1. Dilatometric	40
2. Buoyancy	40
3. Pyknometer	41
4. Sand-cast sphere, cone or cylinder	41
III. Methods and apparatus	42
1. Sand-cast cone	42
2. Determination of the specific volume-temperature curve	42
(*a*) Liquid metal	43
(*b*) Solid metal	45
(*c*) Solidification range	47
IV. Results	48
1. Specific volume-temperature curves	48
V. Discussion	57
VI. Summary	58
VII. Acknowledgments	59
VIII. Bibliography	59

I. INTRODUCTION

1. IMPORTANCE OF PROBLEM

In 1928 the American Foundrymen's Association, through its Committee on Gray Iron Castings, proposed to the Bureau of Standards the desirability of an investigation on the "liquid shrinkage" of

[1] Research Associate representing American Foundrymen's Association.

metals. A research associate was appointed in April, 1929, to work on the investigation.

It was soon evident, however, that the information desired by the practical foundryman involves much more than could properly be included under the term "liquid shrinkage." The foundryman, in producing a satisfactory casting, has a threefold interest in the shrinkage problem—first, he must make the dimensions of his pattern greater than the dimensions of the desired casting; second, he must employ all means possible to attain the maximum density in the casting and to produce a metal free from porosity, piping, and gas holes; third, he must consider the design of his casting in its relation to the propensity of the casting to crack in the mold as a result of stresses set up by differential shrinkage particularly at sharp angles or abrupt changes in cross section.

2. DEFINITIONS AND GENERAL ASPECTS OF SHRINKAGE

When a molten metal or alloy is cooled to ordinary temperature, a change of volume takes place. This change is the summation of three consecutive volume changes which for the purpose of the present paper, are defined as follows:

1. Shrinkage or contraction of liquid metal is the change in volume on cooling from any temperature in the liquid state to some lower temperature in liquid state.

2. Shrinkage or contraction during solidification is the volume change of a pure metal in passing from the liquid state to the solid state at the freezing point, or the change in volume of an alloy in passing from the liquid state at the beginning of the freezing range to the solid state at the end of the freezing range. The shrinkage undergone during solidification of a eutectic or of an inter-metallic compound, freezing at a constant temperature, is similar to that of a pure metal.

3. Shrinkage or contraction of solid metal is the change in volume on cooling from some temperature below its freezing point or range to a lower temperature.

The shrinkage during solidification of an alloy with a freezing range will include, therefore, all three types of shrinkage defined above; that is, liquid, solidification, and solid.

Shrinkage or contraction of the liquid is a definite physical property of a metal or alloy. This value, therefore, is fixed and constant for each metal or alloy. The shrinkage during solidification is essentially a constant for a pure metal, eutectic, or intermetallic compound. However, in alloys of the solid-solution type, the solid metal, which separates from the melt during freezing continually changes in composition and the shrinkage during solidification is correspondingly complicated. During this selective crystallization stresses may be set up on account of the different coefficients of expansion of metal of different composition. According to Davey (1)[2] all crystals are produced in a state of strain.

The volume change of a metal or alloy in the solid state may also be variable. Stresses may exist in a cast alloy of the solid-solution type as the result of progressive solidification and structural trans-

[2] The figures given in parentheses here and throughout the text relate to the reference numbers in the bibliography given at the end of this paper.

formations after solidification. Such stresses may also be due partly to the temperature gradients set up during cooling.

As a result of these stresses in a cast alloy, the observed contraction of a bar, designated as patternmaker's shrinkage, may differ from that which would be calculated from the true thermal expansion of the alloy. In determining the thermal expansion of an alloy, the specimen is heated or cooled as nearly uniformly as possible. The alloy attains equilibrium in temperature and tends to approach equilibrium in composition.

Another factor which influences the difference between the true thermal expansion of a metal or alloy and the pattern-maker's shrinkage is the apparent failure of a casting to register the true shrinkage taking place at and slightly below the freezing point or range. The cause of this may possibly be due to the fact that material at the grain boundaries does not possess sufficient rigidity to register the actual contraction of the grains or crystallites. This situation makes it impracticable to determine the shrinkage or contraction of a solid alloy casting by using thermal expansion measurements.

It is of interest to know the relative tendency of some metals and alloys to distribute their shrinkage between an external pipe and internal voids. Except where conditions are such that a complete rigid shell is formed about a cooling mass of molten metal before the interior has reached the freezing temperature, the shrinkage caused by contraction of the liquid interior will result in a depression in the upper surface (external pipe). Shrinkage that takes place during the change of state may contribute largely to the production of internal voids when such tendency is exhibited by the metal or alloy. This characteristic to form internal voids is not so pronounced in pure metals as it is in some alloys.

The distribution of the shrinkage or contraction during solidification, whether in the form of an external pipe, internal pipe, or small cavities (porosity) throughout the casting, will depend largely on the following factors: (*a*) The amount of shrinkage during solidification; (*b*) the freezing temperature of the metal; (*c*) type of metal, whether it is pure, eutectic, intermetallic compound, solid solution, or any combination of these; (*d*) fluidity of the metal; (*e*) heat conductivity, heat capacity, and pouring temperature of the metal; (*f*) location and design of gates and risers; (*g*) ratio of surface area to volume; and (*h*) heat capacity, heat conductivity, and initial temperature of the mold material.

The first five factors may be grouped as properties of the metal, while the remaining factors may be classed as foundry or casting practice or technique. It is obvious, from the number and complexities of the factors influencing the amount and distribution of the shrinkage in the casting of any particular metal or alloy that it is very difficult, if indeed possible, to determine the influence of all these various factors by means of any single experimental procedure.

II. PREVIOUS METHODS

Methods that have been previously employed for measuring the volume changes undergone by a metal in cooling from the liquid state to room temperature will be reviewed under four headings—dilatometric; buoyancy; pyknometer; sand-cast sphere, cone, or cylinder.

1. DILATOMETRIC

Dilatometric methods consist in observing the change in volume of a given material with change in temperature. In the solid state the specimen is usually in the form of a bar, and the change in volume is calculated from changes in linear dimension measured directly. For observing the change in volume with change in temperature in the liquid state, the molten metal is heated or cooled in a container of known volume calibrated to give directly the corresponding volume change. Such methods were employed by most of the early workers for determining the specific volume of metals in the liquid state. The work of Matuyama is typical (2).

A differential dilatometer was used by Goodrich (3) on a number of low-melting metals and alloys. The metal sample was placed in one of two similar bulbs and the difference in pressures in the bulbs with change in temperature was observed. This method is limited to low-melting-point metals and alloys on account of the lack of suitable materials for containers. The method is also limited by the extreme precautions necessary in guarding against the formation of internal cavities, which appreciably influence the validity of the results.

Benedicks, Berlin, and Phragmen (4) determined the density of molten tin, lead, and low-carbon iron by means of a double manometer, a column of mercury being used as the comparison liquid. Great ingenuity was shown in the construction of U tubes of refractory material capable of retaining the metal and, at the same time, supporting the requisite pressure of nitrogen or other inert gas. This work has recently been continued and extended by Benedicks and coworkers (5) on iron, nickel, and iron alloys in the molten state.

An approximate determination of the "solid" contraction of a cast metal may be made by the method developed by Keep (6), which consisted in measuring the change in length of a cast bar as it cooled from the freezing temperature to room temperature. This method has been extensively used by Turner and his associates (7, 8, 9, 10, 11), Chamberlain (12), Wüst (13), and also by Johnson and Jones (14).

A simplified method used by Anderson (15) for determining pattern-maker's shrinkage consisted in casting a bar in a mold of known length and measuring the length of the resulting bar.

2. BUOYANCY

Buoyancy methods consist in measuring at various temperatures the buoyant effect of an inactive liquid of known density and thermal expansion upon a definite mass of the metal, either liquid or solid, under examination. For lower temperatures an oil is used, while molten sodium chloride or similar salts are used for the higher temperatures.

This method was used by Bornemann and Sauerwald (16), Endo (17, 18), Honda and Endo (19), Russell, Allen, and Goodrich (20), Matuyama (21, 22), and Honda, Kase, and Matuyama (23).

Goodrich (3) has pointed out that the results from this method are subject to several inaccuracies. When investigating low-melting-point alloys and metals, the immersion bath is usually an oil, the density of which changes not only with temperature, but also with time at higher temperature. Correct temperature of the specimen can not readily be obtained at the time of making the determination.

Since the volume changes were always determined during changes of temperature, the temperature of the metal would always lag behind that indicated by the thermometer. Temperature gradients may exist in the heating or cooling bath itself, since stirring is not permissible as this would interfere with the determination of the buoyancy. In a recent article, Matuyama (22) has attempted to meet these criticisms of the method.

In the buoyancy method, as in the dilatometer method, gas bubbles or shrinkage cavities which may form inside the specimen during freezing, would seriously affect the results of a determination of the change in volume during solidification.

Desch and Smith (24) have attempted to determine the density of molten steel by observing the weight of a sinker attached to one arm of a balance in air, in mercury, and in the liquid steel. It is difficult to obtain a suitable sinker that is not attacked by the liquid steel and the mechanical difficulties during the progress of a determination are great indeed.

3. PYKNOMETER

Edwards and collaborators (25, 26, 27) have measured the specific volume of molten aluminum and copper-aluminum alloys by means of a pyknometer, which the authors called a "densimeter." A crucible of known volume was filled with molten metal at a definite temperature and the metal allowed to freeze.

The weight of the resulting ingots and the volumes of the crucibles at the respective sampling temperatures gave information from which the specific volume-temperature curve in the liquid metal was constructed. The method is sufficiently accurate, but like most methods it is applicable only over a limited temperature range.

4. SAND-CAST SPHERE, CONE, OR CYLINDER

Attempts have been made to measure the total shrinkage undergone by cast iron in the liquid state and during solidification by comparing the weight and volume of an "unfed" cast specimen with the weight and volume of a similarly cast but "sound" specimen. The weight of the sound or reference specimen was obtained from a "fed" casting or from the calculated weight of the specimen as determined from the volume and the maximum density of the metal (usually that at the gate). From the difference in weight between the unfed casting and the sound or reference specimen the combined volume change due to the shrinkage of the metal in the liquid state and also the shrinkage taking place during solidification may be determined.

West (28) has reported results on cast iron obtained in this manner. Two spheres of the same dimensions were cast, one being fed from a heavy riser and the other being unfed. The experiments were repeated on spheres of larger sizes. His results were not consistent, however. Smalley (29) conducted similar experiments on conically shaped specimens of gray cast iron, to determine the relation between shrinkage during solidification and the tendency to form a pipe.

Longden (30) has reported results on cylinders and spheres, fed and unfed, and Schwartz (31) cast four spheres from the same runner and calculated the shrinkage from the density of the metal in the gate and the weight and volume of the spheres.

These methods are similar in principle and undoubtedly gave useful results to the foundry in which they were used. However, there is no means of differentiating between the shrinkage of the liquid metal and that occuring during solidification. Furthermore, since feeding occurs during the entire pouring period, it is difficult to determine just what was measured by the foregoing methods.

III. METHODS AND APPARATUS

Two methods were investigated as a means for determining the volume changes occurring when a molten metal is cooled down to ordinary temperature. Attempts were first made to obtain the data from sand-cast cones. It was soon apparent that true values for the shrinkage were not obtainable by this method. Consequently attention was focused upon the investigation of methods for obtaining data from which specific volume-temperature curves could be constructed covering the range from the molten state to room temperature. It was believed that the best evaluation of the different factors constituting the over-all shrinkage from molten metal to solid at room temperature could be obtained from a curve of this type.

1. SAND-CAST CONE

A conical casting, designed to be cast base up, in sand, was first used in an effort to determine the volume changes due to shrinkage in the liquid metal and during solidification. After casting 24 specimens it was obvious that true shrinkage values were not obtained by this method, presumably for the following reasons:

1. The temperature of the metal at the instant the mold cavity is completely filled can not be determined because there is no uniformity of temperature throughout the mass of liquid metal.

2. A volume change takes place in some of the metal during the pouring period as molten metal in contact with the sand surface will receive more or less chill and a solid shell of metal will be formed while the specimen is being poured, thus diminishing the true shrinkage of the casting.

Therefore, no further consideration of this method was given in this investigaton. However, it is realized that a method of this type may be quite useful and satisfactory in further phases of an investigation of this nature when attention is turned to the influence of foundry variables upon the distribution of the types of shrinkage. Further details of this method have been presented in a preliminary report on the investigation (32).

2. DETERMINATION OF THE SPECIFIC VOLUME-TEMPERATURE CURVE

It has already been pointed out that when molten metal is cooled down to the solid state at room temperature, the resulting change in volume is the summation of three successive volume changes, namely, shrinkage of the liquid metal, shrinkage during solidification, and shrinkage of the solidified metal.

In the curve (fig. 1), $V_a - V_b$ represents the change in specific volume with change in temperature of a metal in the liquid state as it cools from some temperature a to the freezing temperature b. The interval $V_b - V_c$ represents the change in specific volume of a metal in

passing from the liquid state at temperature b to the solid state at temperature c. The interval $V_c - V_d$ represents the change in specific volume of the solid metal as it cools from the freezing point c to room temperature d.

The change in volume in per cent for each interval can be calculated from the difference in specific volume for that particular interval, thus $\frac{V_a - V_b}{V_a} \times 100$ is the per cent change in volume due to the metal cooling from temperature a to temperature b in which V_a and V_b represent the specific volumes at these two temperatures. Likewise, the change

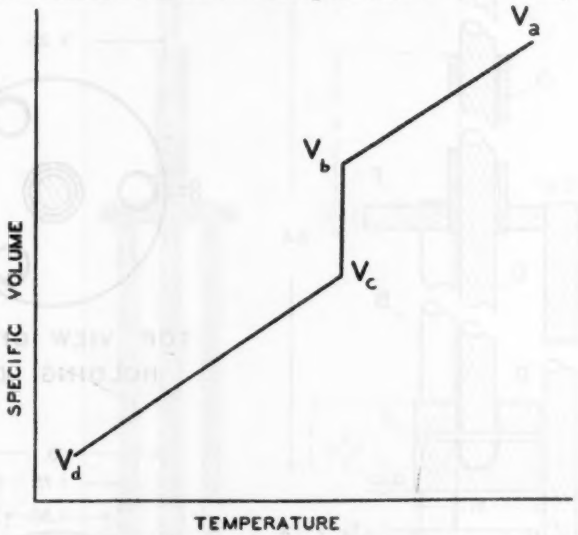

FIGURE 1.—*Typical specific volume-temperature curve of a metal*

in volume, in per cent, due to the shrinkage during solidification is equal to $\frac{V_b - V_c}{V_b} \times 100$, and that due to the shrinkage of the solid metal is equal to $\frac{V_c - V_d}{V_c} \times 100$.

(a) LIQUID METAL

Previous investigators (25) have been able to determine the specific volume temperature relations of molten metals by means of what was essentially the pyknometer method. As pointed out before, the results heretofore reported were limited to the lower melting point metals and alloys. In the present work it was desired to obtain experimental data on cast irons. Hence it was necessary to devise an apparatus which was of such form that it could be built of materials that could be used over a wider range of temperatures than previously used apparatus.

The apparatus as finally used is shown in Figures 2 and 3. It is essentially a pyknometer, but is designated as a "crucible immersion apparatus." The crucible, lid, and supporting rods were made of Acheson graphite.

By means of this apparatus it was possible to isolate a known volume of liquid metal at a definite and predetermined temperature

from a ladle of molten metal. The procedure used was as follows: The crucible was filled by immersing it in a ladle of molten metal and sufficient time was allowed for the crucible to come to the temperature of the surrounding metal or to allow both crucible and metal to cool down to the temperature at which it was desired to obtain a sample. When the desired temperature was reached, the lid was pressed down firmly on the crucible, and the whole assembly removed from the ladle of metal.

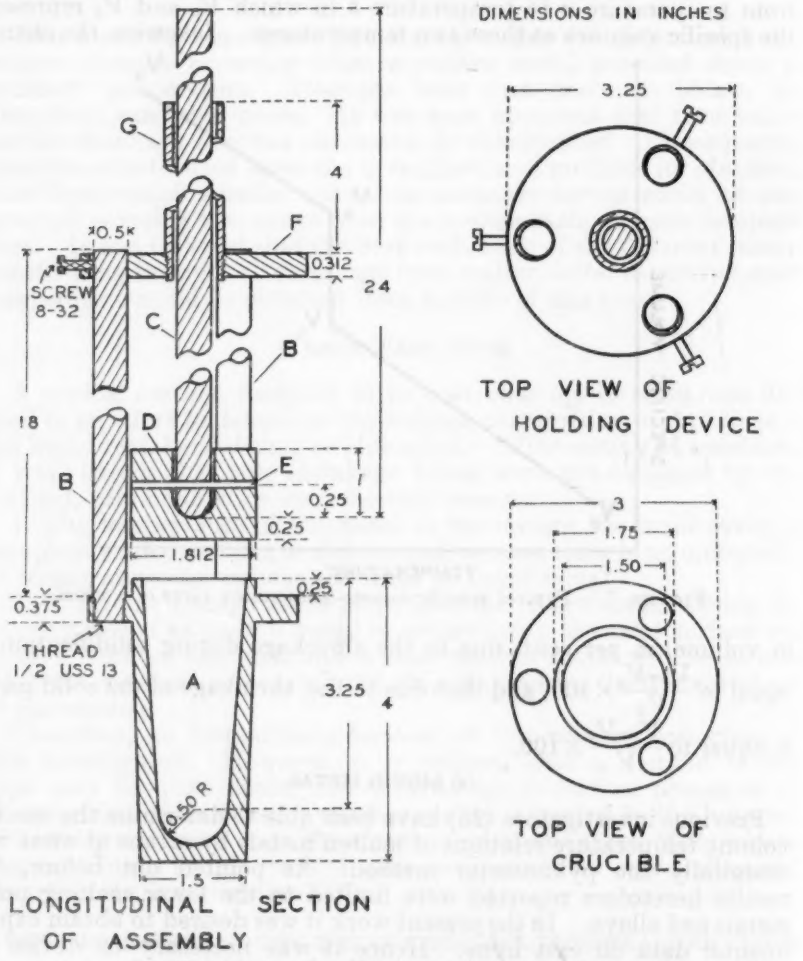

FIGURE 2.—*Crucible immersion apparatus*

A, crucible. *B*, support rods. *C*, control rod. *D* lid. *F*, sustaining pin (4 mm carbon arc rod). *F*, metal base. *G*, metal handle

The sample of metal thus obtained was allowed to freeze within the crucible and to cool to room temperature. Obviously, the mass of the metal did not change on cooling. The resulting ingot was weighed and the specific volume of the metal at the temperature of sampling was calculated by dividing the volume of the crucible at that temperature by the weight of the ingot.

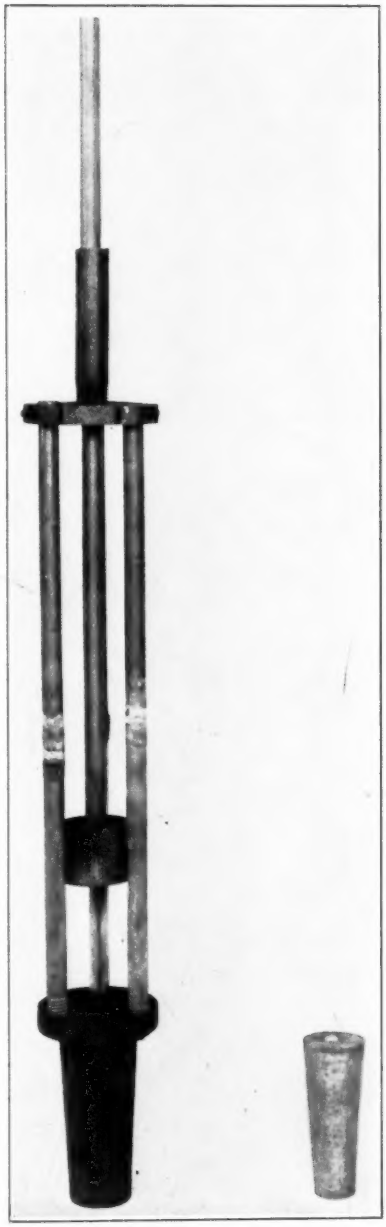

FIGURE 3.—*Crucible immersion apparatus and ingot*

UNIV. OF MICH.

The volume of the crucible at room temperature was determined by weighing the mercury necessary to fill it when the lid was pressed down firmly and the volume at temperatures up to 600° C. was calculated from the thermal expansion of graphite as given by Hidnert and Sweeney (33) up to 600° C. The volumes at temperatures above 600° C. were obtained by extrapolation.[3]

Graphite was found to be entirely suitable for the sampling of all the metals and alloys used with the exception of cast iron. A graphite crucible can not be used for obtaining samples of liquid iron because of the reaction between the iron and the graphite, which changes not only the dimensions of the crucible but also the composition of the iron.

It was found, however, that graphite can be protected from the action of molten cast iron by surfacing it with a refractory "wash." Zirconium oxide powder, to which had been added a small amount of colloidal clay for bond, mixed with water to a "consistency of cream" was found to be very satisfactory. No reaction of the graphite with the oxygen of the air can occur until the device has been removed from the melt. Oxygen may then penetrate through the surface layer and attack the underlying graphite. However, oxidation after removal of the apparatus from the bath does not affect the result.

No difficulty was experienced in removing the resulting ingot from a graphite crucible prepared in the above manner. It was possible to use the same immersion device for subsequent sampling, provided a fresh refractory coating was applied before each immersion. An individual assembly was required for each sample when a number of samples were taken during any particular determination.

The temperature of the molten metal was measured by means of a platinum-platinum rhodium thermocouple within a glazed porcelain protection tube placed inside a graphite tube 1 inch in diameter. The graphite tube was treated with the refractory coating described above when it was to be immersed in cast iron.

(b) SOLID METAL

In addition to determining the specific volume-temperature curve for the liquid metal, it is necessary to determine the same for the metal after solidification. Thermal expansion data for many pure metals are available in the literature, and can be used for determining the specific volume-temperature relations for the solid metal. In the case of gray cast iron, however, thermal expansion data obtained by heating a gray-iron casting would not answer the purpose because it is well known that heating a gray-iron casting results in permanent growth. It was necessary, therefore, to obtain data on the linear contraction of the metal as it cooled from the melt.

The dimensional changes occurring during the cooling of cast iron are affected by the separation of graphite. On freezing and during cooling, the cementite undergoes a partial transformation to ferrite and graphite. Since the specific volume of graphite is approximately

[3] Since the graphite used in the present investigation corresponds to the material investigated by Hidnert and Sweeney in 1927, their data were used for extrapolation instead of the values given by Day and Sosman in 1912 (J. Ind. and Chem. Eng., vol. 4, p. 490; 1912). Day and Sosman obtained lower values for the coefficients of expansion on a graphite rod prepared from one-half inch diameter electrode which was formed from much smaller aggregate particles than the 14-inch electrodes used by Hidnert and Sweeney. The long extrapolation involved in calculating the crucible volumes at elevated temperatures introduces some uncertainty in the specific volumes of the liquid metal.

three times that of cementite, this transformation results in an increase in volume. This increase varies with the amount of cementite decomposed and, therefore, is dependent on the composition of the metal, particularly the carbon, silicon, and manganese contents, and on the rate of cooling of the metal.

The dimensional changes resulting from the graphite separation are affected by everything that affects the cooling rate; that is, pouring temperature, thermal conductivity of the mold and metal, temperature of the mold, size of casting (total heat content), and thickness of cross section. No value for dimensional changes in the solid state should be given for a cast iron without specifying the composition with respect to total and combined carbon.

Data for calculating the changes in specific volume with change in temperature from the solidification temperature to room temperature were obtained by means of observations of the linear contraction of a cast bar as shown in Figure 4. The portion of the bar beyond the

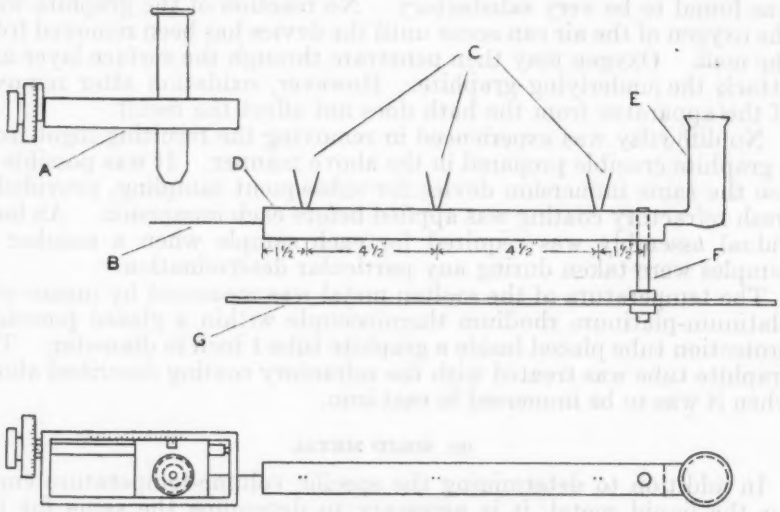

FIGURE 4.—*Apparatus for measuring linear contraction of cast metals*

A, Micrometer slide and microscope.
B, Fused quartz rod.
C, Thermocouples.
D, Shrinkage bar.
E, Pouring gate.
F, Fixed steel pin.
G, Steel plate.

fixed pin can be of any convenient length and the cross section can be made to any convenient dimensions. In this investigation, three different sizes were used, namely, ¾ inch (1.905 cm) square, 1 inch (2.54 cm) square, and 1½ inch (3.81 cm) square, all 12 inches (30.48 cm) long.

A fused quartz rod was used to indicate the linear movement of the cast bar on cooling. The rod was allowed to project into the mold cavity about one-eighth of an inch to insure that it would be firmly gripped by the metal on casting. The coefficient of thermal expansion of fused quartz is much less than that of iron, namely, 0.53×10^{-6}

for fused quartz (35) and 14.7×10^{-6} for iron (36) (between room temperature and 600° C.) The small movement of the cast bar as transmitted through the quartz rod was measured by means of a microscope mounted on a micrometer slide. The mold was made of green sand.

Turner (7), in measuring the total linear contraction of gray cast iron as it cooled from the end of the freezing range to room temperature, used a metal rod to join the movable end of his T bar casting with his measuring device or extensometer. One end of the metal connecting rod was necessarily embedded in the end of the cast-metal bar. In this and subsequent work with this method, no corrections appear to have been made for the linear expansion of the metal connecting rod.

It was essential that the average temperature of the bar be obtained during the cooling interval. In order to secure this, three thermocouples were located in the 12-inch cast bar at distances of 1½, 6, and 10½ inches, respectively, from the free end of the bar. It was assumed that an average of the three temperatures measured in this manner represented the average temperature of the bar. In practice, the three thermocouples, all of the same length and size, were joined in parallel, and the average temperature of all three was obtained by one reading of the instrument. Chromel-alumel thermocouples and a portable potentiometer indicator were used to indicate temperatures. The wires of the thermocouples were insulated from each other and from the molten metal by means of a sodium silicate silica-flour cement. The welded tip of each thermocouple extended into the mold cavity to one-half the thickness of the resulting bar.

The procedure followed in this determination was as follows: A shrinkage bar was cast by pouring metal from a ladle into a green sand mold. The temperature of the cast bar was read simultaneously with the observations on the movement of the quartz rod made by means of the microscope mounted on a micrometer slide. From these data the temperature contraction curve was constructed. The influence of cross-sectional area was studied by comparing data obtained from bars poured simultaneously of different cross-sectional dimensions.

(c) SOLIDIFICATION RANGE

For alloys which do not have a sharp freezing point, it was necessary to determine the liquidus point, the temperature at which incipient crystals form on cooling; and also the solidus point, the temperature at which incipient fusion begins on heating. The interval between these two temperatures is the solidification range. These temperatures were determined by thermal analysis methods.

Cast specimens 5 inches long and 1½ inches in diameter were used. A ⅜-inch hole, 4 inches deep, was drilled along the longitudinal axis of the cylinder into which was inserted a platinum-platinum rhodium thermocouple protected by means of a glazed porcelain tube. The specimen was mounted in a 4-inch coil of a high-frequency induction furnace and the intervening space filled with zircon sand. The electromotive force developed by the thermocouple was measured by means of a potentiometer. The time in seconds required for each successive change of one-tenth millivolt was recorded and inverse-rate heating and cooling curves of the specimen were obtained. The

liquidus point was taken as that temperature at which the first break occurred in the cooling curve, and the temperature of the solidus point as the first break in the heating curve.

IV. RESULTS

1. SPECIFIC VOLUME-TEMPERATURE CURVES

Specific volume-temperature curves were determined for a number of nonferrous metals and cast irons.

The specific volume of liquid aluminum at 770° C. was calculated as follows from experimental data obtained with the crucible immersion apparatus:

Temperature of liquid aluminum at time of sampling	°C	770
Weight of aluminum ingot	g	160.99
Volume of graphite immersion crucible at 20° C	ml	67.64
Average cubical coefficient of expansion of graphite (20° to 770° C.)	$\times 10^{-6}$	10.6
Total change in temperature of graphite crucible heated to sampling temperature (770° to 20° C.)	°C	750
Volume change per milliliter ($750 \times 10.6 \times 10^{-6}$)	ml	0.0080
Volume increase for crucible (67.64×0.0080)	do	.54
Volume of crucible at 770° C. (67.64+0.54)	do	68.18

$$\text{Specific volume of aluminum at 770° C.} = \frac{\text{Volume of liquid Al sample at 770° C.}}{\text{Weight of liquid Al sample at 770° C.}}$$

$$= \frac{\text{Volume of graphite crucible at 770° C.}}{\text{Weight of Al ingot at room temperature}} = \frac{68.18}{160.99} = 0.4235 \text{ ml/g.}$$

In a similar manner, the specific volume of liquid aluminum was determined at other sampling temperatures. By plotting these values against the corresponding temperatures, the upper portion of the curve in Figure 5 was obtained which represents the specific volume of liquid aluminum at various temperatures.

Change of length with temperature measurements were made on a 1-inch square bar of aluminum of 99.2 per cent purity during the period of cooling from its freezing point (658° C.) to room temperature. As may be observed from the lower portion of the curve represented in Figure 5, the solid specific volume-temperature curve tends to flatten out just below the melting point. Possibly this was to be expected, since the cast bar may not have been sufficiently rigid at this high temperature to register the true contraction taking place. For the purpose of this investigation, this condition was overcome by extrapolating the main portion of the curve to the melting point.

The observed linear contraction of the bar, 12 inches long at the casting temperature, from the freezing point to room temperature was 0.213 inch (1.78 per cent) and as corrected for the extrapolated portion, 0.222 inch, or 1.85 per cent.

The cubical contraction of the metal is taken as three times the linear contraction. The value, 5.55 per cent (3×1.85 per cent) represents the decrease in volume undergone by aluminum in cooling from the freezing point to room temperature (20° C.), and agrees closely with the linear contraction of aluminum of the same purity calculated, by extrapolation, from the thermal-expansion data given by Hidnert (37).

The specific volume $\left(\frac{1}{\text{density}}\right)$ of the metal was obtained on the cast

bar after forging. The cross-sectional area was reduced 400 per cent by forging at 400° C. The forged bar was annealed at 450° C. for one hour. The specific volume of a sample cut from this bar was determined as 0.3683 ml/g at 20° C. The corresponding specific volume of aluminum in the solid state at 658° C. is 0.3903 ml/g as computed on the basis of the specific volume of the metal at 20° C. and the contraction of 5.55 per cent occurring in cooling from 658° to 20° C.

By extrapolating that portion of the curve (fig. 5) representing the specific volume of liquid aluminum, to the freezing point (658° C.)

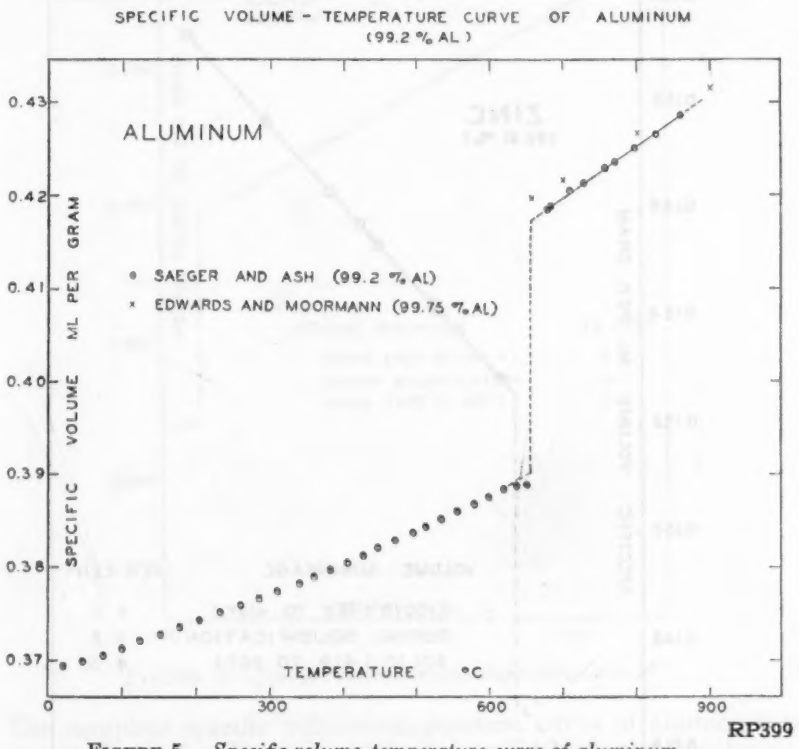

FIGURE 5.—*Specific volume temperature curve of aluminum*

Shrinkage during solidification: 6.5 per cent; solid shrinkage (658° to 25° C.) 5.5 per cent

the specific volume of liquid aluminum at the freezing point was found to be 0.4173 ml/g. The difference between the specific volumes of the solid and liquid aluminum at the freezing point, the change in the specific volume due to solidification shrinkage, is equal to $0.4173 - 0.3903 = 0.0270$ ml/g. This is equivalent to 6.5 per cent, as based on the specific volume of the liquid at the freezing point.

The specific volume-temperature curve for the aluminum in the solid state may also be computed from the coefficient of linear thermal expansion. The average coefficient of linear expansion of aluminum of the purity used in this work was determined by Hidnert (36) as 28.7×10^{-6} for the temperature range from 20° to 600° C. By extrapolating to 658° C., the average coefficient of linear expansion for the

temperature range 20° to 658° C. was found to be 29.0×10^{-6}. This latter coefficient, multiplied by the difference in temperature, times 100, gave the per cent linear contraction of this aluminum in passing from the freezing point at 658° to 20° C. as 1.85 per cent. The value determined by observation of the linear contraction of the cast bar coincides with this value. The calculation of the specific volume of the solid at the melting point has been described previously.

Anderson (15) found his results for the linear contraction of aluminum and many of its alloys varied, as follows: Other conditions

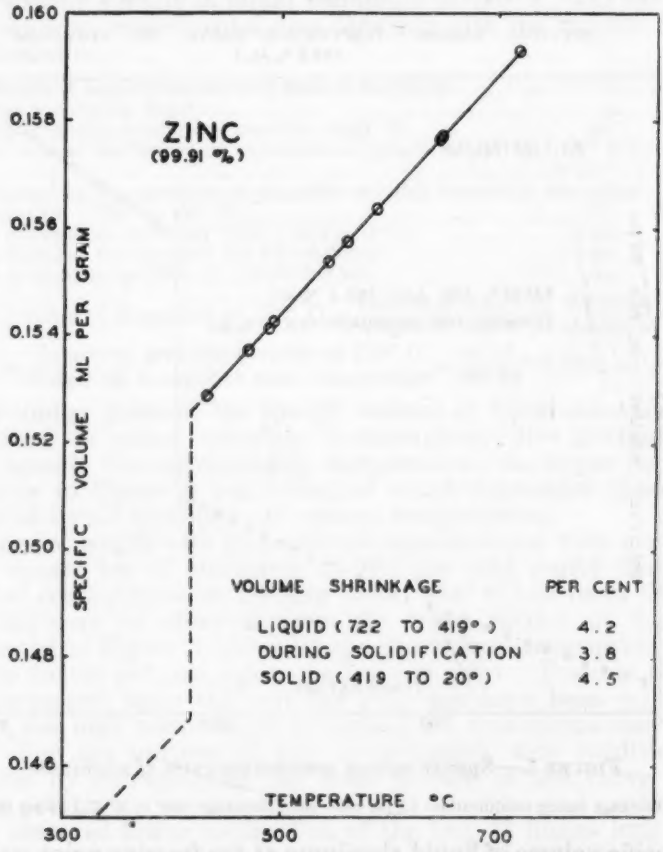

FIGURE 6.—*Specific volume-temperature curve of zinc*

being equal, he found that (*a*) the smaller the cross section of a cast bar of given length, the less the contraction; (*b*) the greater the length for a given cross section, the less the contraction; and (*c*) the contraction was less in chill molds than in sand-cast molds.

Anderson's value for the total linear contraction of commercial aluminum was 1.68 per cent of the length of the solid bar at the freezing point, whereas the value calculated from the thermal expansion measurements of materials of the same purity is 1.85 per cent, as has been shown.

Coleman (38), working with a 90 per cent gold, 10 per cent copper alloy obtained a net casting shrinkage of 1.25 per cent, whereas the contraction of the solid metal calculated from thermal expansion data was 1.62 per cent. Coleman suggested that the variation was probably due to stretching of the casting during cooling as a result of "hanging" to the mold wall or the feeding of metal during the cooling process.

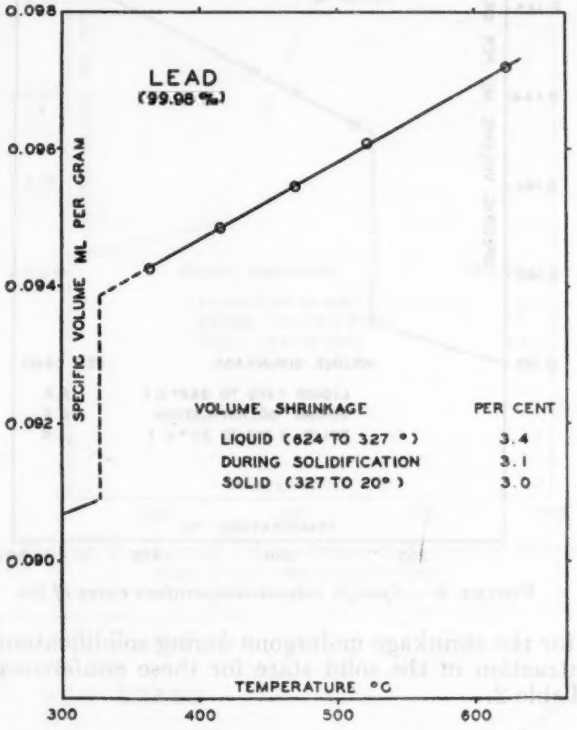

FIGURE 7.—*Specific volume-temperature curve of lead*

The complete specific volume-temperature curve of aluminum is shown in Figure 5. The values reported by Edwards and Moormann (25) are also plotted on this figure for comparison.

By similar procedure, specific volume-temperature curves were determined for zinc, lead, tin, a aluminum-copper alloy containing 8 per cent copper, and red brass of the nominal composition 85 per cent tin, 5 per cent each zinc, lead, and tin. With the exception of aluminum and red brass, the curves representing the specific volume of the solid state have been computed from the thermal expansion data given in the literature. The curves for these various metals are given in Figures 6 to 10, inclusive.

The composition of the different metals and alloys used is given in Table 1.

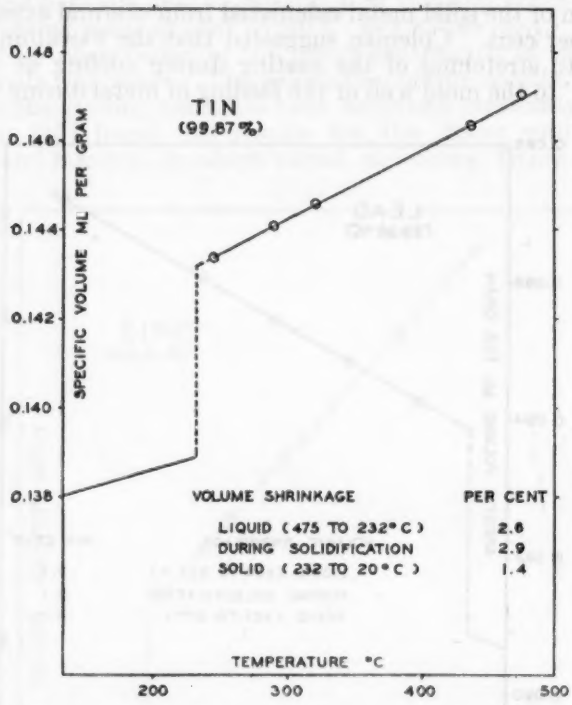

FIGURE 8.—*Specific volume-temperature curve of tin*

Values for the shrinkage undergone during solidification and subsequent contraction in the solid state for these nonferrous metals are given in Table 2.

TABLE 1.—*Chemical composition of nonferrous metals tested*

Material	Composition										
	Cu	Fe	Pb	Zn	Sn	Si	Mn	Mg	Al	Bi	Cd
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*
Commercial aluminum	0.32	0.29	------	None.	------	0.23	0.03	None.	99.16	------	------
Zinc	0.013	0.11	0.059	99.91	------	------	------	------	------	------	0.006
Lead	.01	.01	99.98	------	------	------	------	------	------	None.	------
Tin	.04	.01	.08	None.	99.87	------	------	------	------	------	------
Al-Cu alloy (No. 12)	7.16	.46	None.	------	------	.38	------	------	92.0	------	------
85-5-5-5 (red) brass	84.96	------	4.87	5.15	5.02	------	------	------	------	------	------

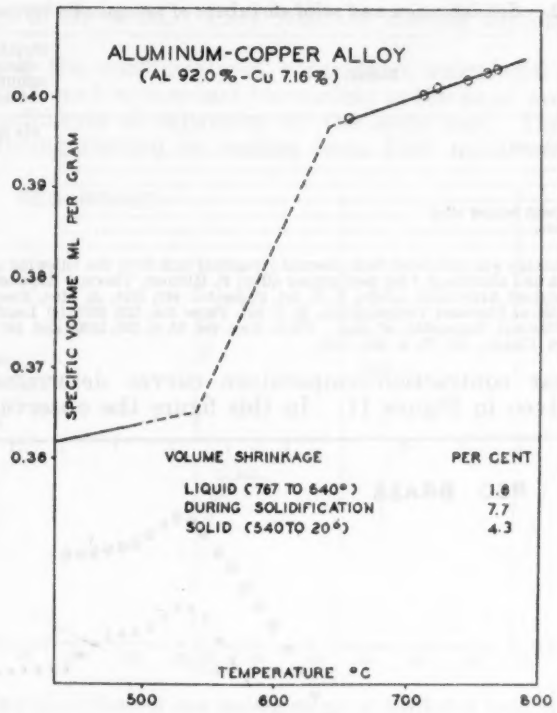

FIGURE 9.—*Specific volume-temperature curve of aluminum 8 per cent copper alloy*

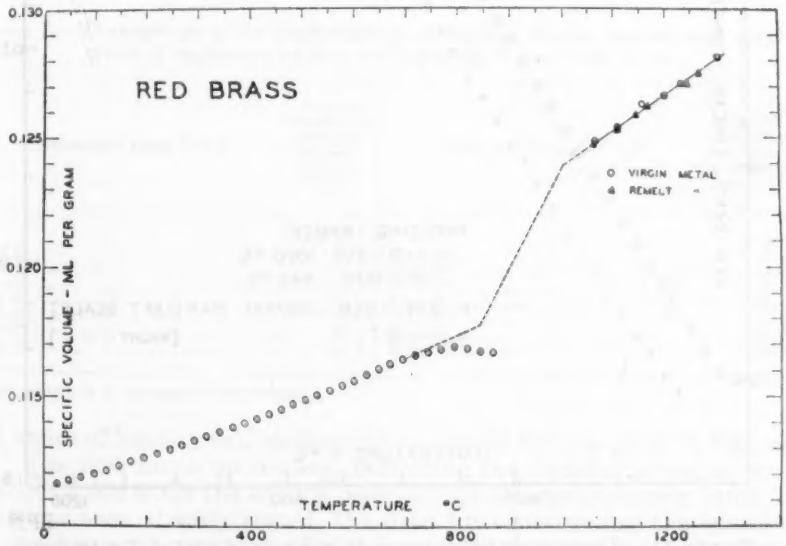

FIGURE 10.—*Specific volume-temperature curve of 85–5–5–5 (red) brass*

Shrinkage during solidification, 5.0 per cent; solid shrinkage (840° to 25° C.), 4.5 per cent.

TABLE 2.—*Solidification and solid shrinkage of several nonferrous metals*

Metal	Shrinkage during solidification	Shrinkage from solidification to 20° C.[1]
	Per cent	*Per cent*
Commercial aluminum	6.5	5.5
Zinc	4.5	3.8
Lead	3.3	2.9
Tin	2.9	1.4
Aluminum 8 per cent copper alloy	7.7	4.3
85–5–5–5 (red) brass	5.0	5.2

[1] The solid shrinkage was calculated from thermal expansion data from the following sources: (*a*) Commercial aluminum and aluminum 8 per cent copper alloy, P. Hidnert, Thermal Expansion of Aluminum and Various Important Aluminum Alloys, B. S. Sci. Paper No. 497; 1924; (*b*) Zinc, Freeman, Sillers, and Brandt. Pure Zinc at Elevated Temperatures, B. S. Sci. Paper No. 522; 1925; (*c*) Lead, P. Hidnert and W. T. Sweeney, Thermal Expansion of lead. Phys. Rev. vol. 35, p. 296; 1930; and (*d*) Tin, Cohen and Olei, Zeit. f. Phys. Chem., vol. 71, p. 385; 1910.

The linear contraction-temperature curves determined for red brass are given in Figure 11. In this figure the observations made

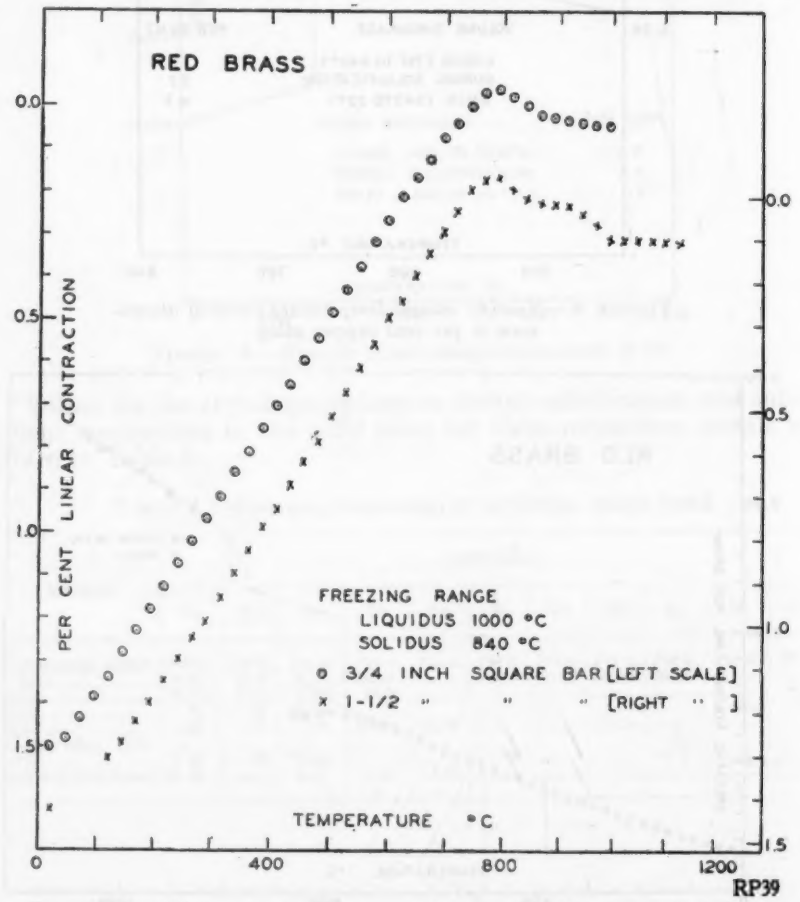

FIGURE 11.—*Linear contraction-temperature curves of 85–5–5–5 (red) brass*

above 800° C. do not strictly represent the linear contraction of the metal because the method used is only adapted for determinations

of shrinkage of the solid. They indicate marked expansion during freezing.

In Table 3 the coefficients of contraction calculated from data obtained on a ¾-inch square cast bar cooling in the sand are compared with the coefficients of expansion on the same bar. The shrinkage occurring during casting in cooling from 700° to 20° C. was 1.41

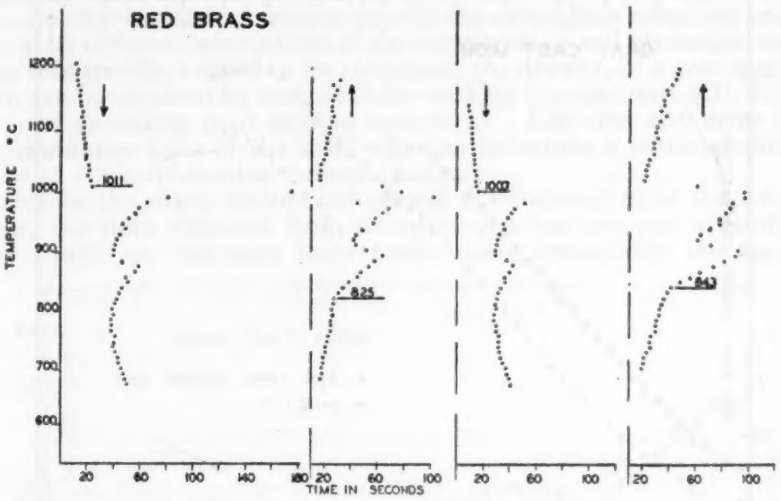

FIGURE 12.—*Heating and cooling curves of 85–5–5–5 (red) brass*

per cent and the expansion on the first heating of the same bar from 20° to 700° C. was 1.40 per cent.

TABLE 3.—*Comparison of the coefficients of contraction during casting and coefficients of expansion on first heating of 85–5–5–5 (red) brass*

Temperature range (° C.)	Average coefficient of linear contraction per ° C.	Temperature range (° C.)	Average coefficient of linear expansion per ° C.[1]
	× 10^{-6}		× 10^{-6}
100 to 20	16.5	20 to 100	17.8
200 to 20	18.4	20 to 200	18.1
300 to 20	19.1	20 to 300	18.5
400 to 20	19.5	20 to 400	18.9
500 to 20	19.8	20 to 500	19.3
600 to 20	20.1	20 to 600	20.0
700 to 20	20.8	20 to 700	20.6

[1] Determined by P. Hidnert, of this bureau.

A series of heating and cooling curves on red brass is given in Figure 12. The first break on cooling, indicating the liquidus point, occurs at about 1,005 while the solidus point occurs at approximately 840° C.

As has been already stated, the data for constructing the specific volume-temperature curve of cast iron must necessarily be obtained for each individual iron studied from the behavior of the solid contraction bars. Figure 13 gives the linear contraction-temperature curves

of two bars for one of the cast irons studied.[4] As the specific volume (or density) of the different cast irons varies with each iron, according to the composition and rate of cooling, the density was determined for each bar. A slice, one-half inch thick, cut from the free end of the expansion bar was chosen as representative of the metal in that bar.

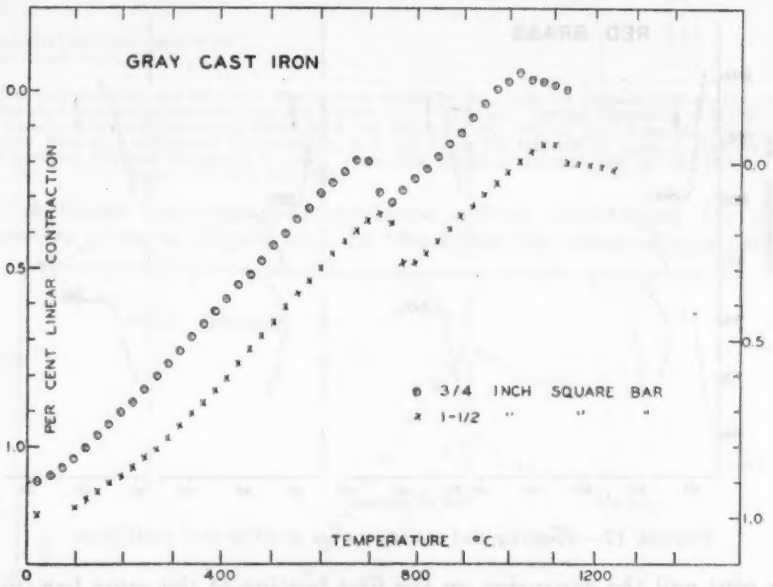

FIGURE 13.—*Linear contraction-temperature curves of gray cast iron*

Analysis: G. C. 2.90; C. C. 0.37; Si 2.87; Mn 0.52; P 0.59; S 0.03 per cent.

Typical results on the specific volume and contraction of a gray cast iron (G. C. 2.90, C. C. 0.37, Si, 2.87, Mn 0.52, and S 0.03 per cent) are given as follows:

Maximum heating temperature		°C	1500
Temperature of liquidus point		per cent	1145
Temperature of solidus point		do	1145
Density at room temperature	¾-inch square bar	g/ml	7.095
	1½-inch square bar	do	7.092
Specific volume at liquidus point		ml/g	0.1441
Specific volume at 1,150° C	¾-inch square bar	do	0.1457
	1½-inch square bar	do	0.1450
Specific volume at room temperature	¾-inch square bar	do	0.1410
	1½-inch square bar	do	0.1410
Average contraction of liquid per 100° C. (1,400°–1,150° C.)		per cent	1.1
Expansion during solidification	¾-inch square bar	do	1.11
	1½-inch square bar	do	0.62
Linear contraction from 1,150° to 25° C	¾-inch square bar	do	1.08
	1½-inch square bar	do	0.83

The specific volume-temperature curve for cast iron was obtained in the manner described above, with the exception that the density at room temperature is that of the metal as cast. A typical curve for gray cast iron is given in Figure 14.

[4] Additional data on the shrinkage of cast iron will be published later.

V. DISCUSSION

The calculated volume change during solidification is dependent upon the value of the specific volume at room temperature. The specific volume of a metal as ordinarily cast in molds may approach but will not coincide with the true specific volume of the metal. It is generally believed that the density of a cast metal is lower than its true density because of minute gaps in the crystalline structure produced by different orientations of the microcrystals and gas inclosures. The true specific volume or its reciprocal, the density, of a cast specimen can be obtained by mechanically working the specimen with subsequent annealing (cast iron an exception). Likewise, any error in the shrinkage data of the solid will also introduce a corresponding error in the solidification volume change.

Due to the many factors influencing the contraction in the solid state, the data obtained from a contraction bar are not absolute. The results on the same irons made under presumably the same

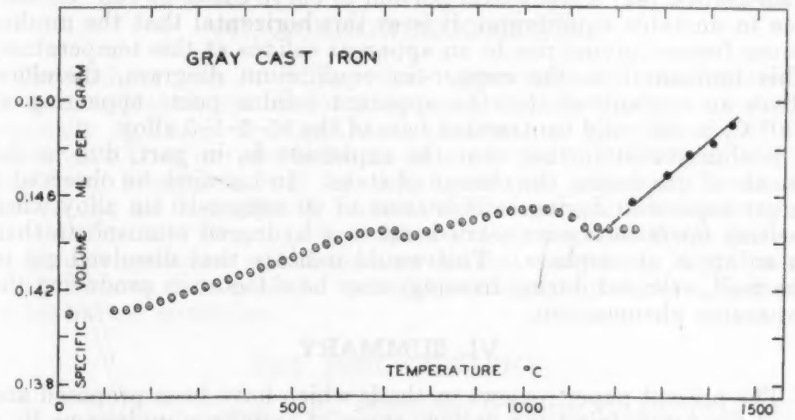

FIGURE 14.—*Specific volume-temperature curve of gray cast iron*

Analysis: G. C. 3.36; C. C. 0.41; Si 2.14; Mn 0.55; P 0.44; S 0.04 per cent

operating conditions vary. Thus, the contraction data presented for cast iron during solidification and for the solid are only relative. It is apparent that the error introduced by using the specific volume of the casting at room temperature, a value that is greater than the true specific volume, reduces the calculated shrinkage resulting from solidification.

The linear contraction-temperature curve of red brass (fig. 11) is somewhat similar in appearance to the curve of gray cast iron in that a marked expansion occurs during solidification. This was more pronounced in the larger bars. For red brass, the expansion begins at approximately 1,000° C. and reaches a maximum at 800° C.

Turner and Murray (8) reported an expansion of pure aluminum during freezing. In the discussion of this paper, Rosenhain pointed out that "once the metal was solid, no doubt the instrument would respond with some considerable degree of accuracy to the expansions or contractions of the metal; but before some sort of more or less rigid connection had been established between the extensometer bar and the fixed pin in the molding flask, he (Rosenhain) could not see what

necessary connections existed between the movements of the extensometer and any volume change."

In a discussion of a paper by Ewen and Turner (9), Desch stated that he agreed that the volume would vary in proportion to the length after the bar was once solidified. He also suggested that any observed expansion during solidification may be due to crystal thrust.

Chamberlain (12) studied a series of copper-aluminum alloys with respect to their behavior during solidification by means of an apparatus similar to Turner's. He found a distinct relationship between the expansion curve during solidification and the crystallization interval curve. He states that the expansions are produced by forces of considerable magnitude.

Sauerwald (39) found a marked expansion for copper and copper-tin alloys during solidification.

Boehm (40) studied the phenomenon of expansion during solidification of copper-tin alloys and the influence of gas atmosphere. He pointed out that in the copper-tin equilibrium diagram of Bauer and Vallenbruck (41) a horizontal portion of curve exists at 798° C. and, due to unstable equilibrium, it is at this horizontal that the mother liquor freezes, giving rise to an apparent solidus at this temperature. This horizontal in the copper-tin equilibrium diagram, therefore, offers an explanation for the apparent solidus point appearing at 800° C. in the solid contraction bars of the 85–5–5–5 alloy.

Boehm stated further that the expansion is, in part, due to the release of gas during the change of state. In his work he observed a larger expansion during solidification of 90 copper-10 tin alloy when melting operations were carried out in a hydrogen atmosphere than in an argon atmosphere. This would indicate that dissolved gas in the melt, released during freezing, may be a factor in producing the expansion phenomenon.

VI. SUMMARY

The present paper reviews methods which have been proposed and used for determining the various types of shrinkage undergone by a cooling metal; defines the three types of shrinkage to be considered—shrinkage of liquid metal, shrinkage during solidification, and shrinkage of the solid metal; and considers in detail two experimental methods, namely, the sand-cast-cone method and the method depending on the determination of the specific volume-temperature relations of the metal.

Reliable shrinkage data were not obtained by use of the sand-cast-cone method, for the following reasons: (*a*) The temperature of the metal at the instant the mold cavity is completely filled can not be determined, since there is no uniformity of temperature throughout the mass of metal in the mold cavity; (*b*) a volume change takes place in a portion of the metal within the mold cavity (due to chilling of the metal along the sand surfaces) during the period of pouring the casting, and a certain amount of feeding of the casting has taken place before the mold cavity has filled with metal.

2. The second and more accurate experimental method used is that which depends upon the construction of the specific volume-temperature curve for the metal under consideration. The specific-volume temperature curve for liquid metal was constructed from data secured by filling a crucible of known volume with the liquid metal at a known

temperature. Since the mass of the sample of liquid metal is the same as that of the sample at room temperature, the liquid specific volume can be readily calculated.

3. Data on the contraction of the solid metal were obtained by direct observations of the change in length with change in temperature of a sand-cast bar of metal. The difference between the specific volume of the solid metal and of the liquid metal at the melting point is the shrinkage resulting during solidification. In the case of an alloy, shrinkage during solidification occurs over a range of temperature. The freezing range of alloys was determined by heating and cooling curves.

4. Typical experimental data and calculations are given, and shrinkage values for the metal in the liquid state, during solidification, and the solid state were determined for commercial aluminum, red brass (85–5–5–5) and a cast iron. Shrinkage of the liquid metal and shrinkage during solidification have also been determined for an aluminum 8 per cent copper alloy, and for lead, zinc, and tin.

VII. ACKNOWLEDGMENTS

The authors wish to express their appreciation to the American Foundrymen's Association for their cooperation in this investigation, especially to Dr. J. T. MacKenzie, chairman of the Committee on Research. They are also indebted to a number of individuals of the Bureau of Standards staff for their assistance, especially to Louis Jordan for his suggestions, advice, and constructive criticism; to Lemuel D. Jones for preparing molds and castings; to W. F. Roeser for his able assistance on the work on thermal analysis; to E. L. Peffer for his work on density of the various specimens; and to Peter Hidnert for his valued criticisms.

VIII. BIBLIOGRAPHY

1. W. P. Davey, A Theory of the Mechanism of Crystal Growth, Phys. Rev., vol. 29, p. 206; 1927.
2. Y. Matuyama, On the Density of Molten Metals and Alloys, Sci. Repts., Tohoku Imperial University, vol. 18, p. 19; 1929.
3. W. E. Goodrich, Volume Changes During the Solidification of Metals and Alloys of Low Melting Point, Trans., Faraday Soc., vol. 25, p. 531; 1929.
4. C. Benedicks, D. W. Berlin, and G. Phragmen, A Method for the Determination of the Specific Gravity of Liquid Iron and Other Metals of High Melting Point, Iron and Steel Inst., Carnegie Scholarship Memoirs, vol. 13, p. 129; 1924.
5. C. Benedicks, N. Ericsson and G. Ericson, Bestimmung des Spezifischen Volumes von Eisen, Nickel und Eisenlegierungen im geschmolzenen Zustand, Archiv für das Eisenhüttenwesen, vol. 3, p. 473; 1930.
6. W. J. Keep, Cooling Curves and Tests for Cast Iron, J. Iron and Steel Inst., vol. 48, p. 227; 1895.
7. T. Turner, Volume and Temperature Changes During the Cooling of Cast Iron, J. Iron and Steel Inst., vol. 69, p. 48; 1906.
8. T. Turner and M. T. Murray. The Copper-Zinc Alloys—A Study of Volume Changes, J. Inst. Metals, vol. 2, p. 98; 1909.
9. D. Ewen and T. Turner, Shrinkage of Antimony-Lead Alloys and of Aluminum Zinc Alloys During and After Solidification, J. Inst. Metals, vol. 4, p. 128; 1910.
10. A. Hague and T. Turner, The Influence of Silicon on Pure Cast Iron, J. Iron and Steel Inst., vol. 82, p. 72; 1910.
11. J. L. Houghton and T. Turner, Volume Changes in Alloys of Copper with Tin, J. Inst. of Metals, vol. 6, p. 192; 1911.

12. J. H. Chamberlain, A Study of Volume Changes in Alloys. J. Inst. Metals, vol. 10, p. 193; 1913.
13. F. Wüst, Shrinkage of Metals and Alloys, Metallurgie, vol. 6, p. 769; 1909.
14. F. Johnson and W. G. Jones, New Forms of Apparatus for Determining the Linear Shrinkage and for Bottom-Pouring of Cast Metals and Alloys, Accompanied by Data on the Shrinkage and Hardness of Cast Copper-Zinc Alloys. J. Inst. of Metals, vol. 28, p. 299; 1922.
15. R. J. Anderson, Linear Contraction of a Series of Brasses and Bronzes, Trans. Am. Fdymen's Assn., vol. 31, p. 371; 1923; and Linear Contraction and Shrinkage of a Series of Light Aluminum Alloys, Trans. Am. Fdymen's Assn., vol. 31, p. 392; 1923.
16. K. Bornemann and F. Sauerwald, Density Measurements of Metals and Alloys. Zeit. f. Metallkunde, vol. 14, p. 145; 1922.
17. H. Endo, On the Measurement of Change of Volume During Solidification, Sci. Repts., Tohoku Imp. Univ., vol. 13, p. 193; 1924.
18. H. Endo, On the Volume Change in Alloys During Solidification, Sci. Repts., Tohoku Imp. Univ., vol. 13, p. 219; 1924.
19. K. Honda and H. Endo, On the Volume Change in Cast Iron During Solidification, Sci. Repts., Tohoku Imp. Univ., vol.16, p. 19; 1927.
20. Russell, Allen, and Goodrich, British Nonferrous Metals Research Association Report, Ser. 85; 1925.
21. Y. Matuyama, On the Volume Changes in Certain Type Metals During Solidification, Sci. Repts., Tohoku Imp. Univ., vol. 17, p. 1; 1928..
22. Y. Matuyama, On the Volume Change of Manganese During Solidification, Sci. Repts., Tohoku Imp. Univ., vol. 18, p. 733; 1929.
23. K. Honda, T. Kase, and Y. Matuyama, On the Change of Volume of Cast Iron During Solidification, Sci. Repts., Tohoku Imp. Univ., vol. 18, p. 699; 1929.
24. C. H. Desch and B. S. Smith, Interim Report on the Density of Molten Steel. J. Iron and Steel Inst., vol. 119, p. 538; 1929.
25. J. D. Edwards and F. A. Mooremann, Density of Aluminum from 20° to 1,000° C., Chem. & Met. Eng., vol. 24, p. 61; 1921.
26. J. D. Edwards, Mechanism of Solidification of a Copper-Aluminum Alloy, Chem. & Met. Eng., vol. 24, p. 217; 1921.
27. J. D. Edwards and H. T. Gammon, Causes of Piping in Aluminum Ingots, Chem. & Met. Eng., vol. 24, p. 338; 1921.
28. Thomas D. West, Molders' Text Book, John Wiley & Sons, p. 6; 1909.
29. O. Smalley, Volume Changes of Cast Iron on Solidification, Inst. of Brit. Fdymen., vol. 16, p. 405; 1922–23.
30. J. Longden, Some Considerations on Liquid Shrinkage in Gray Cast Iron, Inst. of Brit. Fdymen., vol. 18, p. 573; 1924–25.
31. H. A. Schwartz, Shrinkage in White Cast Iron, Trans. Am. Fdymen's Assn., vol. 37, p. 205; 1929.
32. C. M. Saeger and E. J. Ash, Methods for Determining the Volume Changes Undergone by Metals and Alloys during Casting, Amer. Foundrymen's Association, vol. 38, p. 107; 1931.
33. P. Hidnert and W. T. Sweeney, B. S. Tech. Paper No. 335; 1926.
34. N. L. Bowen, J. W. Greig, and E. G. Zies, Mullite, a Silicate of Alumina, J. Wash. Acad. Sci., vol. 14, p. 206; 1927.
35. W. Souder and P. Hidnert, B. S. Sci. Paper No. 524; 1925.
36. W. Souder and P. Hidnert, B. S. Sci. Paper No. 433; 1921.
37. P. Hidnert, Thermal Expansion of Aluminum and Various Important Aluminum Alloys. B. S. Sci. Paper No. 497; 1924.
38. R. L. Coleman, Physical Properties of Dental Materials (Gold Alloys and Accessory Materials), B. S. Jour. Research, vol. 1, (RP 32); December, 1928.
39. F. Sauerwald, Einiges über die Schwindung der Metalle Zeit. f. Metallkunde, vol. 21, p. 293; 1929.
40. F. Boehm, Ueber die Schwindung von Legierungen, Dissertation, Technischen Hochschule zu Breslau; 1930.
41. Mitt. a. d. Mat.-Prüf.-Amt., Berlin; 1922.

WASHINGTON, October 22, 1931.

RP400

REGISTRATION OF CATHODE RAYS BY THIN FILMS OF METALS AND METAL COMPOUNDS

By Warren W. Nicholas and C. G. Malmberg

ABSTRACT

A search was made for a method of registering cathode rays analogous to the photographic method which could be carried out entirely in daylight and in which no development process would be required. For this purpose, thin metal films (Pb, Ag, Bi, Sn, Cd, As, Cu, Sb, Zn, Mg, Se) were deposited on glass by evaporation from a coiled tungsten filament in vacuum. These were then exposed, in vacuum, to a beam of 10 kv cathode rays. Films of Pb and Sn so thin as to be quite transparent before exposure, were darkened to a density of the order of 0.5 by exposure to 0.01 coulomb/cm^2. Also opaque films of the above metals were exposed to the vapors of various acids (HCl, HNO_3, HBr, HI, H_2S, H_2SO_4); this generally produced a lowered opacity, in many cases the films becoming quite transparent. Exposure to cathode rays tended to restore the original opacity. In general, the best effects were obtained with nitrates and bromides; $Bi(NO_3)_3$ seemed to show the most promise as to sensitivity and permanence of the record. The cathode ray bombardment caused practically all the films to fluoresce, the color and intensity of the fluorescence depending on the material.

CONTENTS

	Page
I. Introduction	61
II. Experimental method	62
III. Observations	64
1. Opaque metallic films	64
2. Transparent metal films	64
3. Films of metal compounds	64

I. INTRODUCTION

In a previous investigation[1], in which very thin beaten gold foils were suspended in a vacuum and bombarded with cathode rays, it was noticed that the region of the foil struck by the cathode rays gradually became less transparent to visible light, and under continued bombardment became quite opaque. The gold foils used were about 0.09 μ thick, and the voltages, current densities, and times were of the order of 30 kv, 0.1 ma cm^{-2}, and 10 hours, respectively. The color of the transmitted light appeared to acquire a slight bluish tinge in the bombarded films, and spectral transmission measurements[2] between 440 mμ and 680 mμ showed that the transmission was lowered by the greatest factor in the red and by the least in the vicinity of the original transmission maximum at 500 mμ. The colors of the reflected light from the two portions of the films seemed identical, but spectral photometric comparison was not resorted to here. The me-

[1] W. W. Nicholas, B. S. Jour. Research, vol. 2 (RP60), p. 837: May, 1929.
[2] These measurements were kindly performed by Dr. Deane B. Judd of the colorimetry section.

chanical structure of the foils was somewhat changed as was evidenced by a fine wrinkling of the thin foils in the region bombarded.

Several workers have observed effects on metals which may well be related to the above phenomena. Webster and others [3] have observed a discoloration of beryllium, and of thin silver films deposited on beryllium, when used as anticathodes in an X-ray tube. Coblentz and Hughes [4] observed a differential condensation of moisture for the parts of metal surfaces exposed to ultra-violet light over long periods and the parts not so exposed. Eder [5] has reviewed similar effects for sunlight. It was to have been expected that bombardment by cathode rays would produce similar surface effects; this has been verified for a large number of metals by both Carr [6] and the writers. Carr investigated the condensation of a variety of vapors on surfaces of metals which had been exposed to cathode rays in air, or to low-speed electrons in vacuum, and discovered that in many cases mercury vapor causes a very clear development of the exposed region.

A consideration of the above observations suggested the possibility that many substances not appreciably sensitive to visible light may be capable of registering cathode rays in a way analogous to the ordinary photographic method. Further, the work on gold foils indicated that some of these materials might give a permanent record without the necessity of any development process to bring out a latent image. Since, for an investigation now in progress, such a process of registration of cathode rays was urgently required, a search was made of a considerable number of substances which it was thought might prove suitable for the purpose. Some of the results of this search are presented here.

II. EXPERIMENTAL METHOD

It is very advantageous in studying such effects as are described above to use thin films of material deposited on a transparent backing, such as glass. Since even moderately high-speed cathode rays can penetrate only a few microns of most solids, there should be no advantage in using greater thicknesses of the sensitive material. Metal deposits may readily be made by evaporation from a coiled tungsten filament in vacuum.[7] [8] [9] [10] Such films are very uniform, clean, smooth, and their thickness can be accurately controlled, thus allowing any changes in optical transmission properties to be readily studied. Films of various compounds of these metals can be made by exposing the metal films to various acid vapors for a period of several hours. Many of these compounds are practically completely transparent; such compounds are, of course, especially favorable for the purpose at hand.

The apparatus used in the present investigation is outlined in Figure 1. Electrons, supplied by a tungsten filament *F* behind a narrow slit in a copper shell *C*, were accelerated in the space between *C* and *A*, and passed through a slit in *A* into the brass box *B*. There

[3] Webster, Clark, Yeatman, and Hansen, Proc. Nat. Acad. Sci., vol. 14, p. 679; 1928.
[4] W. W. Coblentz and C. W. Hughes, Science, vol. 60, p. 64; 1924; B. S. Sci. Paper No. 493, vol. 19, p. 577; 1924.
[5] J. M. Eder, Handbuch der Photographie. Heft 2, Band 1, 2 Teil, 3 Aufl., (Photochemie) pp. 118, 396 1906.
[6] P. H. Carr, Rev. Sci. Inst., vol. 1, p. 711; 1930.
[7] See footnote 3, p. —.
[8] A. H. Pfund, Phys. Rev., vol. 35, p. 1434; 1930.
[9] B. S. Circular, No. 389; 1931.
[10] Cartwright and Strong, Rev. Sci. Inst., vol. 2, p. 189; 1931.

they were deflected by a magnetic field to cause them to strike the various prepared plates P mounted on N; this permitted making a number of exposures with a single pumping of the apparatus. N was a cylindrical brass tube with numerous springs similar to S mounted along the upper edge; these springs performed a double duty as clamps and electrical contacts to the sensitive surfaces of P. A slot cut in the side of N permitted the entrance of the electron beam. This

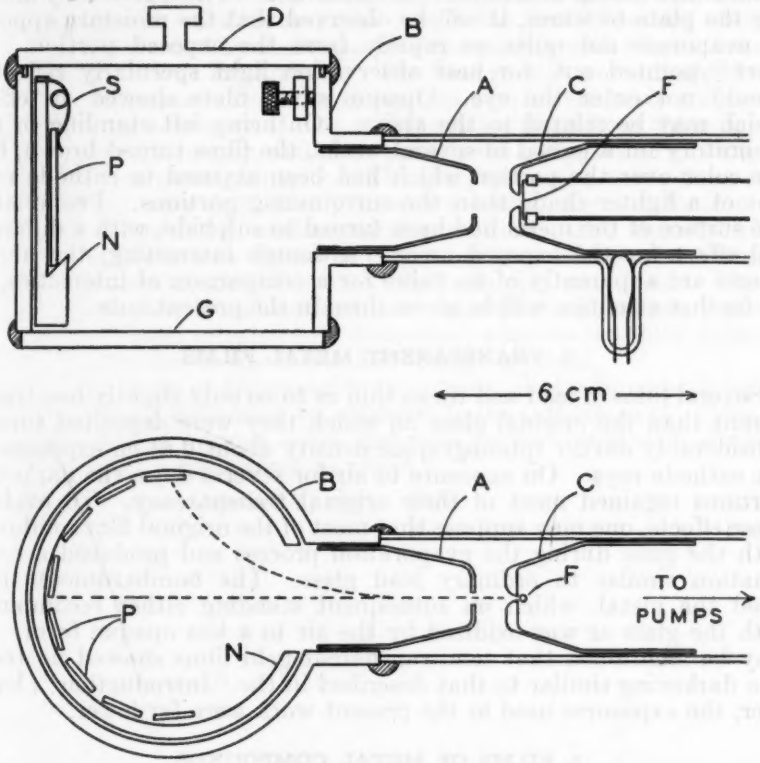

FIGURE 1.—*Apparatus for testing the registration of cathode rays by various substances*

beam had a cross section of about 1 cm by 2 mm when it struck the plates. B was closed at one end with a glass plate G, for visual observation, and at the other end by a brass cover which could be removed for replacements of plates P. Sealing wax was used for the vacuum joints. The tube was evacuated with a mercury vapor pump and Hyvac. Only constant d. c. potentials were used on the tube. Breakdown usually occurred at about 40 kv. Only 10 kv cathode rays were used in the present experiments, and the exposure used with all the films was about 0.15 coulombs/cm^2.

III. OBSERVATIONS

1. OPAQUE METALLIC FILMS

Opaque films of Pb, Ag, Bi, Sn, Cd, As, Cu, Sb, Zn, Mg, and Se showed, without exception, after bombardment, the differential condensation of moisture referred to above. The best way to observe this phenomenon is to gradually cool the plate until an opalescent film of moisture is seen to condense on its surface. Then, gradually allowing the plate to warm, it will be observed that the moisture appears to evaporate not quite so rapidly from the exposed portion. As Carr [11] pointed out, for best observation light specularly reflected should not enter the eye. Opaque silver films showed an effect which may be related to the above. On being left standing in the laboratory for a period of several weeks, the films turned brown, but the color over the portion which had been exposed to cathode rays was of a lighter shade than the surrounding portions. Presumably the surface of the metal had been turned to sulphide, with a differential effect for the exposed areas. Although interesting, the above effects are apparently of no value for a comparison of intensities, so no further attention will be given them in the present note.

2. TRANSPARENT METAL FILMS

Several films of lead and tin so thin as to be only slightly less transparent than the original glass on which they were deposited turned considerably darker (photographic density about 0.5) on exposure to the cathode rays. On exposure to air for several days, the darkened portions regained most of their original transparency. To explain these effects, one may suppose that most of the original film combined with the glass during the evaporation process and produced a combination similar to ordinary lead glass. The bombardment then freed the metal, which on subsequent standing either recombined with the glass or was oxidized by the air to a less opaque form. It may be mentioned that semitransparent gold films showed no trace of a darkening similar to that described in the "Introduction"; however, the exposures used in the present work were far lower.

3. FILMS OF METAL COMPOUNDS

These films showed the greatest promise for the permanent registration of cathode rays. Each of the metals listed above was exposed to the vapor of each of the following acids: HCl, HNO_3, HBr, HI, H_2S, and H_2SO_4. Other metal films were heated in air in order to form the oxides. The nitrates and bromides were generally the most sensitive to cathode ray bombardment in that they formed the strongest images. Bismuth nitrate, which was originally transparent, gave especially dark images (photographic density of the order of 1) but no exact significance can be assigned to the comparison with other metals without a better knowledge of their comparative thicknesses. Generally, the color of the bombarded portion was brown, with a metallic appearance, but this was not always the case. The most striking exception was with ZnI, which was originally fairly

[11] See footnote 6, p. 62.

transparent but which was changed by the bombardment to a brilliant orange color.

Permanence of the images was not tested over very considerable periods. Many of them faded in a few hours on being left standing in the laboratory. However, many of the records, especially with Bi, Sn, and Cd persisted over a period of weeks; this is more than adequate to obtain permanent photographic or photometric records.

It is important, before using any substance for actual work, to investigate the conditions under which the best films are obtained. This was indicated by some special experiments with films of bismuth nitrate of various thicknesses. The best results were obtained when the films were made from metal deposits which were fairly transparent (say, having a density of 0.5). The nitrate films from these deposits gave sharper, stronger, and more permanent images than did the films from opaque metal deposits. The images on the thick films sometimes faded very appreciably in a few hours, whereas those on the thin films persisted unchanged for months. The density of the images with the thin films was of the order of 1 for current densities of 0.01 coulombs/cm^2, when 10 kv cathode rays were used. The thin films were smooth and uniform and somewhat opalescent, especially if they had been nitrated in a desiccator, whereas the thick films were less uniform due to the formation of large crystals.

With only one or two possible exceptions, all the films, both metallic and otherwise, fluoresced on exposure to the cathode rays. The fluorescence was in various colors and with various intensities, the colors ranging from a deep green to violet.

WASHINGTON, October 7, 1931.

EFFECT OF CASTING TEMPERATURES AND OF ADDITIONS OF IRON ON BEARING BRONZE (Cu 80:Sn 10:Pb 10)

By C. E. Eggenschwiler [1]

ABSTRACT

A study was made of the effect of different casting temperatures (1,850° to 2,120° F.) and of additions of iron (from 0 to 1.0 per cent) upon the hardness, the structure, and resistance to wear, to pounding, and to single-blow impact of a bearing bronze containing 80 per cent copper, 10 per cent tin, and 10 per cent lead.

In general, increasing the casting temperature from 1,850° to 2,120° F. increased the resistance to wear, increased the grain size with only a slight effect on the distribution of the lead, and slightly decreased the Brinell hardness. The resistance to pounding was increased within the casting range of 1,900° to 2,000° F. and the notch toughness decreased on the bronzes cast close to 2,000° F.

Additions of iron exceeding 0.3 per cent proved detrimental. Smaller additions of iron decreased the resistance to wear and increased the Rockwell and Brinell hardness. Additions of iron up to 1.0 per cent increased the resistance to pounding. Increasing the iron content above 0.3 per cent produced segregation of the lead particles, decreased the grain size, and decreased the notch toughness

CONTENTS

	Page
I. Introduction	67
II. Preparation of the castings	68
III. Test methods	69
IV. Results and discussion	70
1. Effect of casting temperature	70
(*a*) Structure	70
(*b*) Resistance to wear	71
(*c*) Resistance to pounding	72
(*d*) Resistance to single-blow impact	72
(*e*) Hardness	72
2. Effect of additions of iron	73
(*a*) Structure	73
(*b*) Resistance to wear	74
(*c*) Resistance to pounding	75
(*d*) Resistance to single-blow impact	75
(*e*) Hardness	75
V. Summary and conclusions	76
1. Effect of casting temperature	76
2. Effect of additions of iron	77
VI. Acknowledgments	77

I. INTRODUCTION

The effects of varying compositions upon the properties of bronze bearing metals have been previously reported from the Bureau of Standards in three papers.[2 3 4] As a continuation of this work, the

[1] Research Associate representing The Bunting Brass & Bronze Co., Toledo, Ohio.

[2] H. J. French, S. J. Rosenberg, W. LeC. Harbaugh and H. C. Cross, Wear and Mechanical Properties of Railroad Bearing Bronzes at Different Temperatures, B. S. Jour. Reasearch, vol. 1 (RP13); 1928.

[3] E. M. Staples, and H. J. French, Bearing Bronzes with and without Zinc, B. S. Jour. Research vol. 2 (RP68); 1929.

[4] E. M. Staples, R. L. Dowdell and C. E. Eggenschwiler, Bearing Bronzes with Additions of Zinc, Phosphorus, Nickel, and Antimony, B. S.Jour. Research, vol. 5 (RP205): 1930.

present paper reports the effects of variations in casting temperature and of the addition of varying amounts of iron upon the properties of an 80–10–10 bearing bronze (80 per cent copper, 10 per cent tin, and 10 per cent lead). This particular alloy was chosen for study because it has been used for many years as an all-round general bearing bronze. The fact that the tin content of this alloy is close to the eutectoid composition of tin in copper (12.5 to 13.0 per cent), that the lead content is sufficient for ample study of its distribution throughout the copper-tin matrix, and that the alloy presents no hazards in founding and machining, made this alloy an excellent one for the proposed experiments.

It is the general opinion that iron has a deleterious effect upon bearing bronzes and especially upon leaded bronzes.[5] Since the use of virgin metals is not economical, small amounts of iron are almost always found in the finished casting. This minor constituent of bronze makes its way into the metal through the use of iron or steel stirrers, contaminated machine-shop products, and through the reclamation of unserviceable and "worn out" bronze bearings.

In the founding of brass and bronze, it is seldom possible to pour all castings at the same temperature. It has been shown by Carpenter and Elam,[6] Karr,[7] and Rowe [8] that variations in the casting conditions may appreciably affect the properties of the bronze or brass.

This investigation forms one phase of the study of bearing bronzes which has been in progress for the last three years in cooperation with the Bunting Brass & Bronze Co. on the research associate plan.[9]

II. PREPARATION OF THE CASTINGS

Two sets of test castings were prepared for study, only virgin copper, tin, and lead being used. The first set of castings was poured at different temperatures into test castings. The second set of castings, which was poured at a constant temperature, contained additions of iron up to 1 per cent. The chemical composition of the various test castings and the casting temperatures employed are given in Table 1.

In order to approximate the structure and the properties of the bushing bearings generally used in the automotive and allied industries, the test castings were of relatively thin section. Castings for wear-test specimens were hollow cylinders, while those used for impact, pounding, and hardness tests were in the form of plates as described in previous papers.[10] The method of casting and gating employed was typical of that used in brass and bronze foundries at the present time.

---

[5] S. L. Hoyt, Metallography: Part II. The Metals and Common Alloys, p. 125. McGraw-Hill Book Co.
[6] H. C. H. Carpenter and Miss C. F. Elam, Causes of Unsound Castings of Admiralty Bronze, J. Inst. Met., vol. 19, p. 155; 1918.
[7] C. P. Karr, Standard Test Specimens of Zinc Bronze, B. S. Tech. Paper No. 59; 1916.
[8] F. W. Rowe, The Effect of Casting Temperature on the Physical Properties of a Sand-Cast Zinc Bronze, J. Inst. Met., vol. 31, p. 217; 1924.
[9] B. S. Circular No. 296.
[10] See footnotes 3 and 4, p. 67.

TABLE 1.—*Chemical compositions and pouring temperatures of the bronzes studied*

Alloy No.	Casting temperature	Chemical composition				Alloy No.	Casting temperature	Chemical composition			
		Copper	Tin	Lead	Iron			Copper	Tin	Lead	Iron
	°F.	Per cent	Per cent	Per cent	Per cent		°F.	Per cent	Per cent	Per cent	Per cent
5	1,850	81.4	10.2	8.5		50	2,000	79.9	9.9	10.1	0.01
2	1,920	81.3	9.3	9.4		80	2,000	80.0	9.3	10.4	.10
1	2,000	78.4	9.5	12.1		60	2,000	79.8	9.7	10.1	.31
3	2,040	81.5	8.8	9.7		70	2,000	79.7	10.0	9.8	.51
4	2,120	81.4	8.8	9.7		40	2,000	78.9	9.9	10.1	1.02

NOTE.—These analyses were made by L. M. Long, plant metallurgist, at the chemical laboratory of the Bunting Brass & Bronze Co., Toledo, Ohio.

Separate melts were made for each casting temperature and for each test casting containing an addition of iron. The weight of the metal in each heat was 35.5 pounds, consisting of 28.5 pounds of copper, 3.5 pounds of tin, and 3.5 pounds of lead. All melting was done in a gas-fired crucible furnace.

The casting procedure was as follows: The copper (and iron, when this element was added) was melted under a slag of glass and a mixture of sodium carbonate and borax. The tin and lead were added after the charge had become molten and some of the slag was then removed. After a short reheating period, the melt was removed from the furnace, skimmed free of slag, stirred, and cast into sand molds equipped with core strainers in the pouring gates. The iron additions consisted of very thin, cleaned iron strips and small iron brads. Due to some of the iron brads becoming entangled in the glass slag during melting, the iron content was always slightly lower than that anticipated.

In the process of casting, it was noted that as the temperature of the melt was lowered to about 1,850° F. the metal became sluggish and some difficulty was experienced in obtaining a complete set of test castings. No difficulty was experienced in pouring the test castings at 2,000° F. However, examination of the wear-test castings containing 0.5 and 1.0 per cent of iron, after removal from the sand molds, showed that these castings should have been poured at a higher temperature as a few cold shuts were observed.

The casting temperature measurements were made with a chromel-alumel thermocouple and a portable potentiometer. The chromel-alumel thermocouple was incased in a glazed porcelain tube which, in turn, was inclosed in a graphite tube. Readings were taken in the crucible immediately before pouring.

III. TEST METHODS

It was not the purpose of the present investigation or of the methods of test employed to parallel ideal conditions of bearing service, but rather to show what may be expected when design and lubrication are at fault. The character of the bearing metal is of vital importance when good service conditions begin to fail.

With only one exception, the methods of test employed in this investigation were similar to those described in previously reported bearing bronze studies [11] and the reader is referred to these studies

[11] See footnotes 2, 3, and 4, p. 67.

for complete information on the testing apparatus, test castings, and test specimens.

In addition to the method of wear testing previously described,[11] wear tests were also made on the Amsler machine under low loads in the presence of kerosene. In these "wet" wear tests a stream of kerosene was allowed to flow between the steel and the bronze test specimen. The kerosene prevented surface films from forming by keeping the specimens cool and washing away any small particles of material produced by the abrasion of the wearing surfaces. By means of suitably calibrated springs the pressure between the wear test specimens could be varied to give any desired value. The apparatus equipped for wear testing in the presence of kerosene and its description is given in Figure 1.

All of the "dry" wear tests were made under a load of 37.5 pounds (the dead weight of the head of the Amsler machine) corresponding to a maximum pressure of 31,000 lbs./in.^{2} as calculated by Hertz's theory. It should be noted that Hertz's theory becomes inaccurate as soon as the material is stressed beyond the proportional limit. The actual stresses would be considerably smaller. In all of the wear tests the bronze specimen was mounted on the lower spindle of the machine. The "wet" wear tests were made under loads of 5 and 10 pounds, corresponding to maximum pressures of 10,000 and 12,000 lbs./in.^{2}. Since the value of the proportional limit of 80–10–10 bronze as usually determined is slightly higher than 12,000 lbs./in.^{2}, the stresses induced in the bronzes during the "wet" wear tests did not exceed the proportional limit.

The other tests made were Rockwell and Brinell hardness, pounding, and Izod impact (single blow). These tests were made at room temperature, 350° and 600° F.

IV. RESULTS AND DISCUSSION

1. EFFECT OF CASTING TEMPERATURE

The effect of casting temperature on thin-walled castings is more noticeable than on thick-walled castings. The casting temperature of large castings containing appreciable amounts of lead should be low enough to produce rapid cooling of the metal and so entangle the lead before it has an opportunity to settle out or segregate. The quick freezing of leaded bronzes does not necessarily offer a solution for lead sweating, but there will be less lead sweat with low pouring temperatures. It is to be expected and has been previously confirmed by investigators that the rate of cooling as well as the type of mold used will have an appreciable effect upon the properties of the finished casting.[12] [13]

(a) STRUCTURE

Visual examination of the etched specimens without magnification showed a grain size which increased as the casting temperature increased. Specimens cast at 1,850° F. had a fine grain size while specimens cast at 2,120° F. had a coarse columnar grain.

---

[11] See footnotes 2, 3, and 4, p. 67.

[12] H. C. Dews, The Effect of Casting Temperatures on the Physical Properties of Nonferrous Alloys, Met. Ind., London, vol. 25, Nov. 21, 1924, p. 498.

[13] J. W. Bolton and J. A. Weigland, Incipient Shrinkage in Some Nonferrous Alloys, Tech. Publ. No. 163, A. I. M. M. E., 1929.

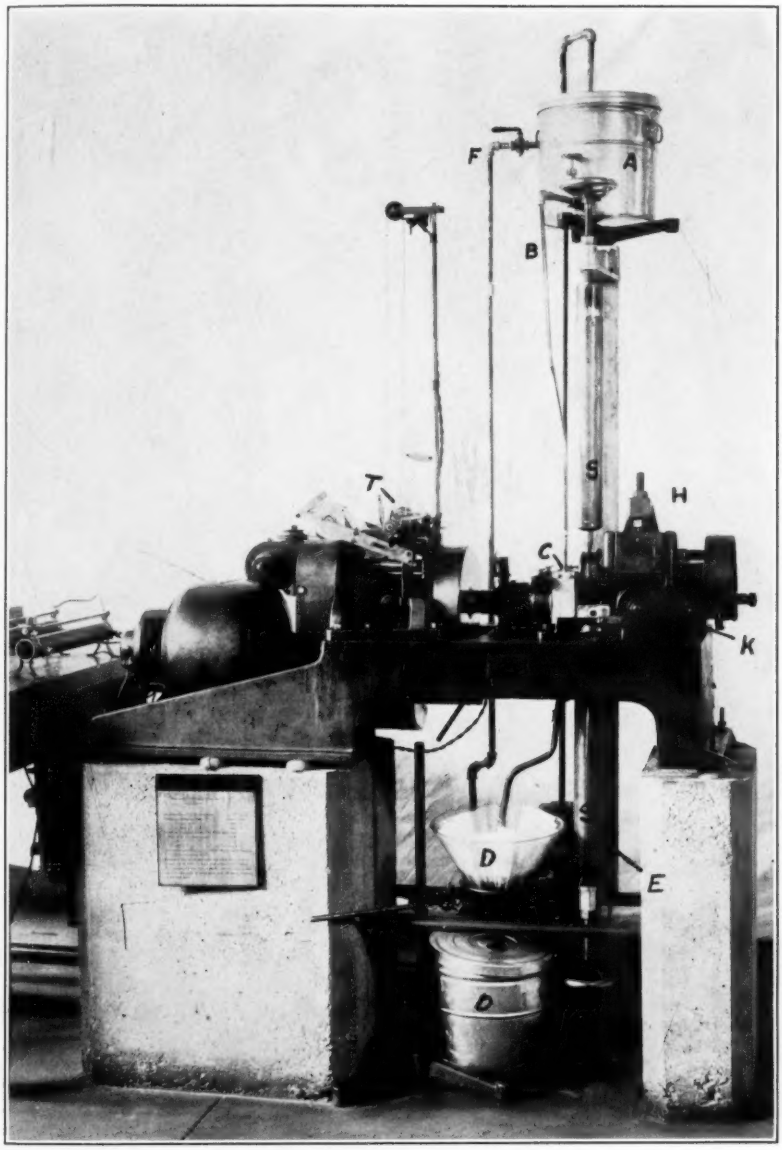

FIGURE 1.—*Amsler machine adapted to the determination of resistance to wear in the presence of kerosene*

C, Specimens; *T*, friction dynamometer; *S'*, equalizing spring to offset weight of head *H*; *S*, calibrated spring for adjusting pressures between test specimens; *D*, filter and reservior for reclaiming kerosene; *E*, pump for transmitting reclaimed kerosene back to reservoir *A* through pipe *E*; *F*, overflow pipe for maintaining a constant head of kerosene in *A*.

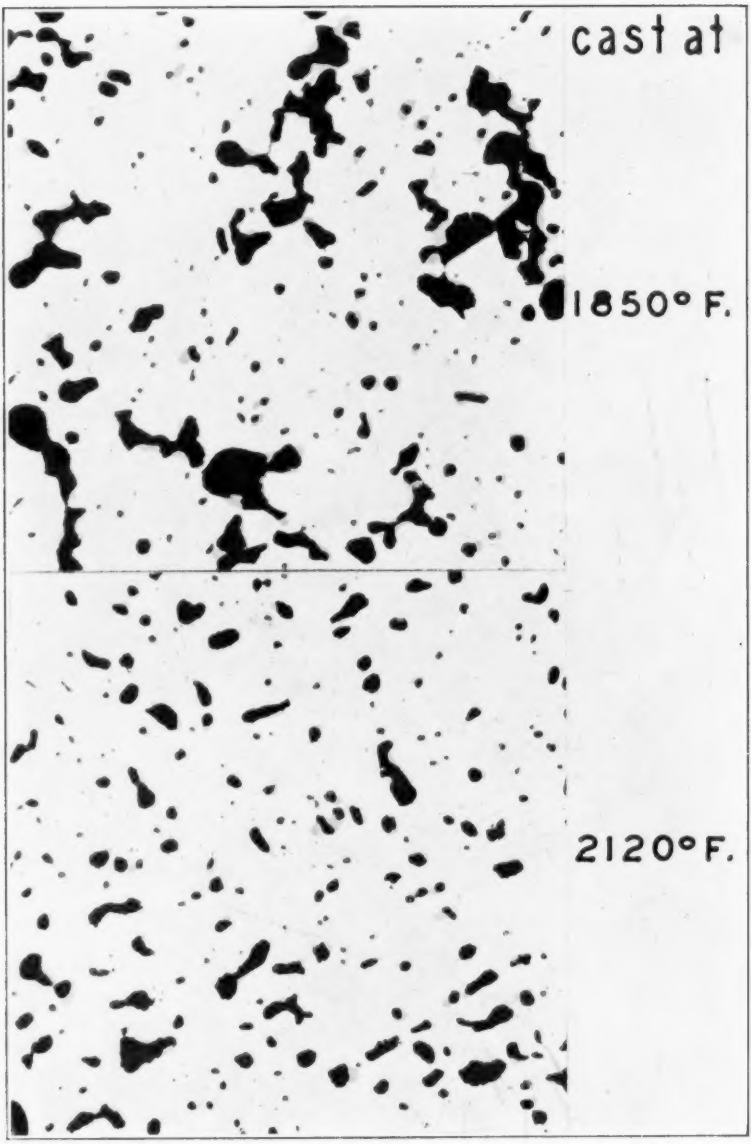

FIGURE 2.—*Distribution of lead in 80–10–10 bronze cast at various casting temperatures. Not etched.* × *100*

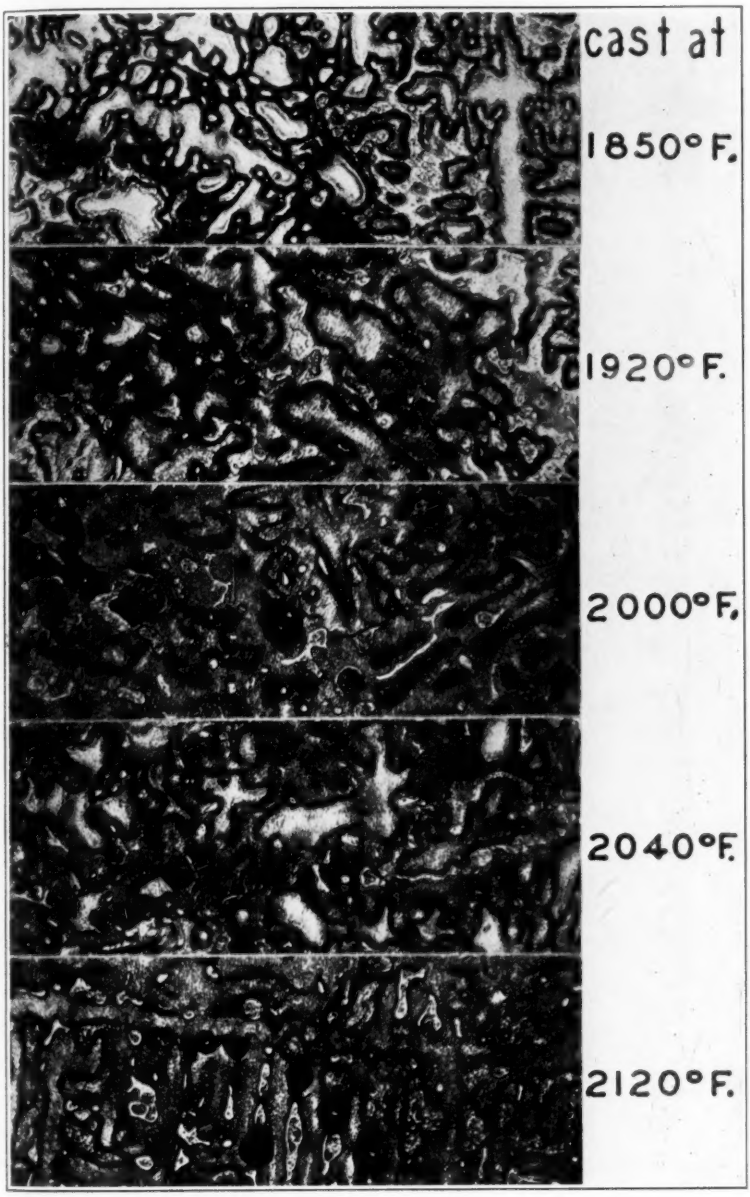

FIGURE 3.—*Microstructure of 80–10–10 bronze cast at various temperatures.*
× 100

Etched with solution of 3 parts of NH_4OH plus 1 part H_2O_2 followed by solution of $FeCl_3$ in HCl (10 g $FeCl_3$ plus 30 ml concentrated HCl plus 120 ml H_2O)

The effect of casting temperatures upon the lead distribution and structure of the bronzes studied is shown in Figures 2 and 3.

No marked differences in the distribution of the lead particles (the black areas in fig. 2) were noticed in specimens cast between 1,850° and 2,040° F. In the specimens cast at 2,120° F., the lead particles were quite uniformly distributed and of rather smaller size.

The etched structures of the bronzes cast at different temperatures (fig. 3) are typical of a copper-tin-lead alloy. The hard delta constituent is shown in relief in the copper-tin-solid solution matrix. Practically no difference can be seen on the etched structures of the bronzes cast at different temperatures.

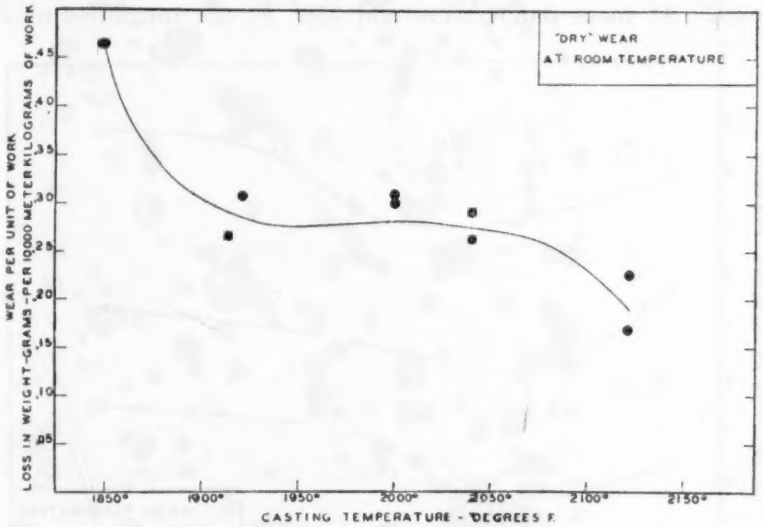

FIGURE 4.—*Effect of casting temperature on the wear resistance of 80–10–10 bronze*

(b) RESISTANCE TO WEAR

In studying the resistance to wear of the bronzes cast at various temperatures, the specimens were run "dry" on the Amsler wear-testing machine. Tests were conducted at room temperature and at 350° F. Because of the difficulties caused by film formation in the tests made at 350° F., none of the results of these tests are given. Figure 4 gives the results obtained at room temperature. It will be noted from this figure that the bronze cast at a low temperature (1,850° F.) shows a high rate of wear. Intermediate casting temperatures gave somewhat lower rates of wear while the highest casting temperature (2,120° F.) resulted in a marked decrease in the rate of wear. In general, it may be said that the rate of wear per unit of work decreased with higher casting temperatures. The preceding statement is in keeping with results previously obtained on the rate of wear per unit of work of sand-cast and chill-cast specimens, which showed that the rate of wear increased with decreased grain size.[14]

[14] See footnote 2, p. 417 of Research Paper No. 13 (vol. 1); 1928.

(c) RESISTANCE TO POUNDING

The effect of casting temperature on the resistance to deformation under pounding is shown in Figure 5. Tests made at room temperature, 350°, and 600° F. indicated that the bronze specimens cast at 1,920° F. deformed the least.

(d) RESISTANCE TO SINGLE-BLOW IMPACT

In Figure 6 are given the results of Izod impact tests on bronzes cast at different temperatures. At all test temperatures (room temperature, 350°, and 600° F.) the test specimens representing the highest casting temperature (2,120° F.) has the greatest resistance to Izod impact. At room temperature and 350° F. the toughness of the

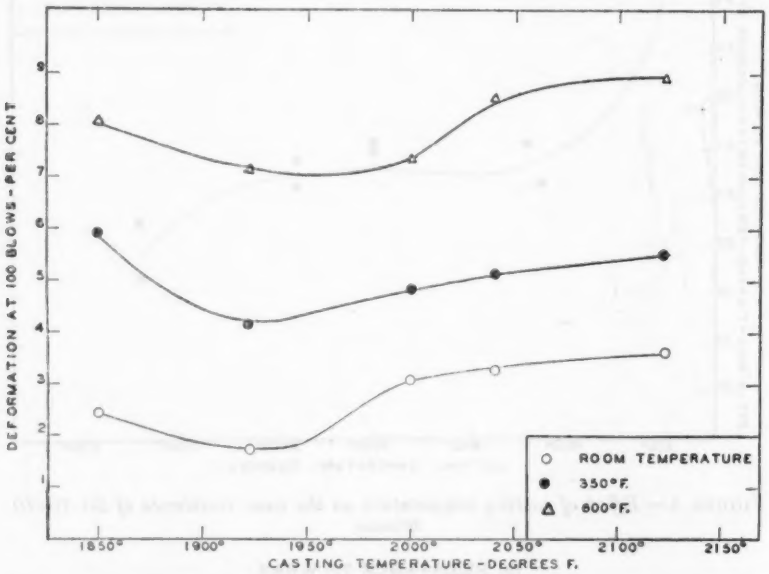

FIGURE 5.—*Effect of casting temperature on the resistance to deformation under pounding at various temperatures on 80–10–10 bronze*

test specimens decreased with increasing casting temperatures up to 2,000° F. An increase in the casting temperature above this point resulted in a rapid increase in the Izod impact resistance. In the tests made at 600° F., the impact resistance increased gradually with increasingly high casting temperatures. The effect of the temperature of test upon the notch toughness was very noticeable. A test temperature of 350° F. resulted in a comparatively small lowering of the impact resistance while a test temperature of 600° F. lowered the impact resistance to a small fraction of its value at room temperature.

(e) HARDNESS

The effect of casting temperatures on the Brinell hardness of the bronzes studied was slight. Figure 6 shows that increasing the casting temperature resulted in only a slight lowering of the hardness.

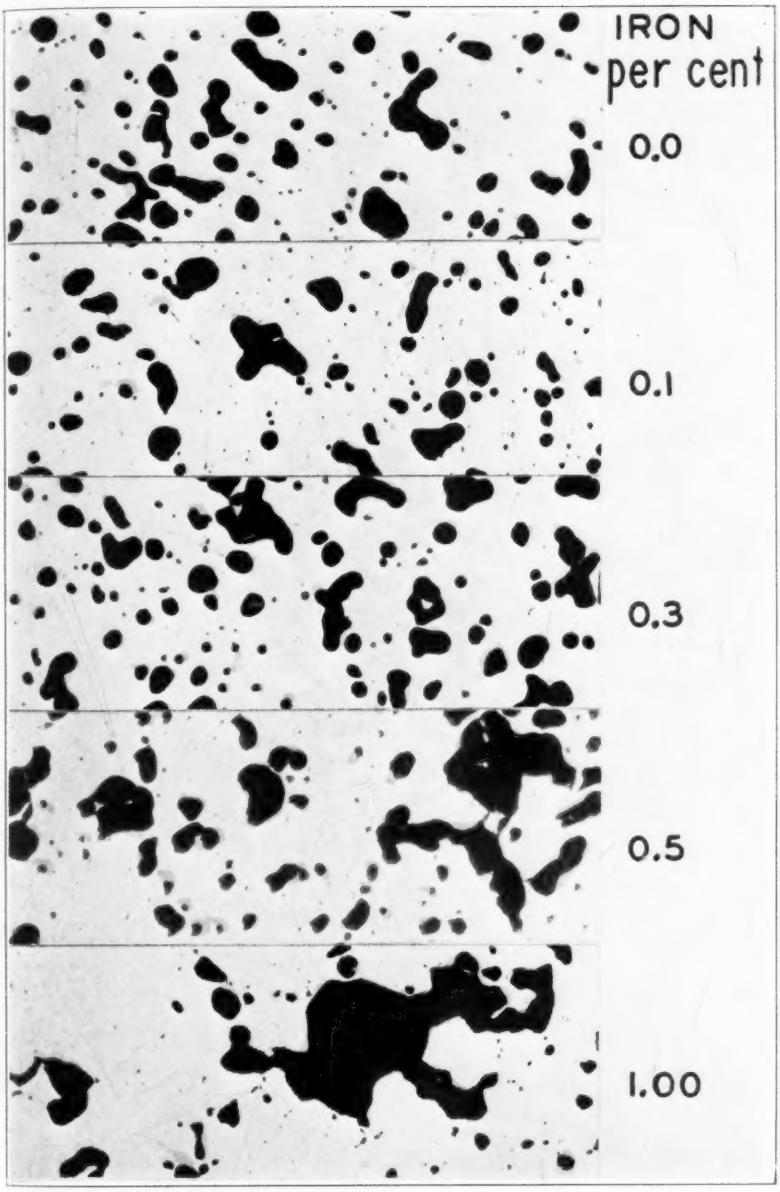

FIGURE 7.—*Distribution of lead in 80–10–10 bronze containing additions of iron. Not etched.* × *100*

UNIV OF MICH

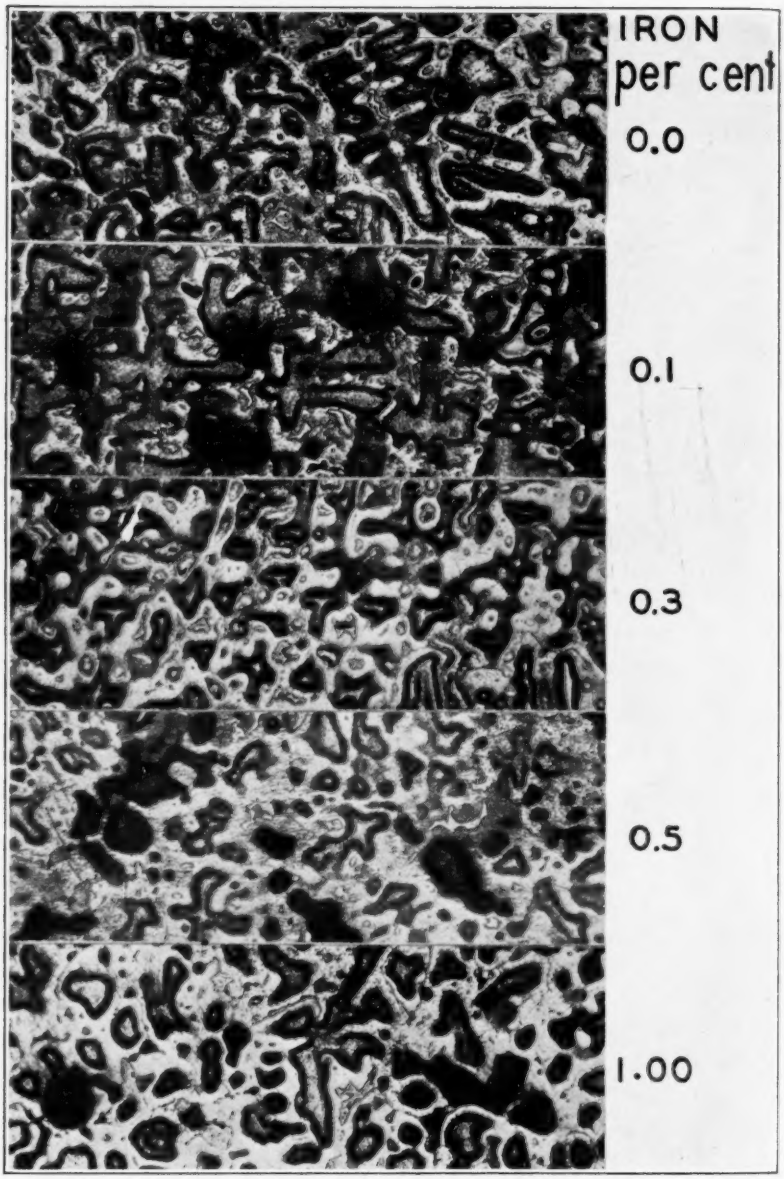

FIGURE 8.—*Microstructure of 80–10–10 bronze with iron additions.* × *100*

Etched with solution of 3 parts NH_4OH plus 1 part H_2O_2 followed by solution of $FeCl_3$ in HCl (10 g $FeCl_3$ plus 30 ml concentrated HCl plus 120 ml H_2O).

2. EFFECT OF ADDITIONS OF IRON

The addition of iron to brass and bronze is considered with favor by some and with equal disfavor by others with the result that many opinions have been expressed on the subject. It has been rather clearly shown by various investigators that additions of iron to brass produce greater hardness, tensile strength, and toughness.[15 16 17 18] The addition of iron to bronze is not considered so favorably. According to Hoyt [15] and Evans,[16] iron may be present up to 0.3 or 0.4 per cent in solid solution and not materially affect the mechanical properties. Hoyt reports that additions of iron above 0.3 per cent render gun metal brittle, but increase the hardness and tensile strength. Iron is also added to copper-lead bearing alloys to prevent the liquation of the lead.[15] Carbon-free iron additions do not produce the undesirable results in brass and bronze that are attributed to iron

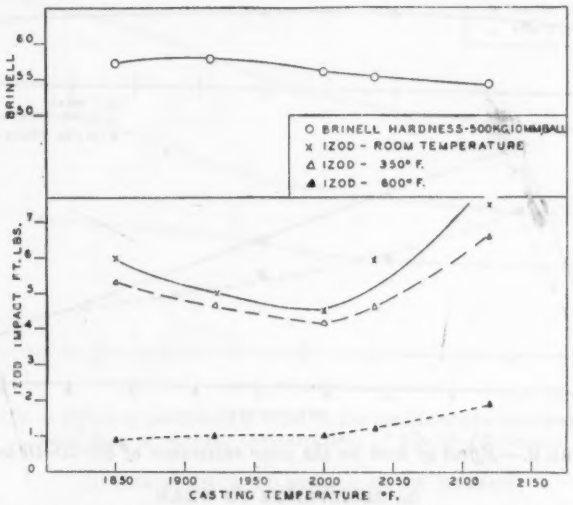

FIGURE 6.—*Results of Brinell hardness and single-blow impact tests at various temperatures on 80–10–10 bronze cast at different casting temperatures*

additions in the form of steel. This is believed to be due to the ease with which practically pure iron is taken into solution as compared with the difficulty of bringing about complete solution of the steel in molten brass and bronze. [19]

(a) STRUCTURE

Visual examination of the polished and etched bronze specimens revealed that the grain structure was normal and typical of sand-cast bronze in the specimens containing up to 0.3 per cent iron. The grain size was slightly larger in the specimens containing 0.1 and 0.3 per cent iron than in the iron-free bronze. The specimens containing 0.5

[15] S. L. Hoyt, Metallurgy. Part III. The Metals and Common Alloys, pp. 123, 125, 128. McGraw-Hill Book Co.; 1921.
[16] U. R. Evans, Metals and Metallic Compounds, (book) Longman, Green & Co., N. Y., vol. 4, p. 61; 1923.
[17] O. Smalley, Effect of Iron on Brass, Met. Ind., vol. 17, p 421; 1920.
[18] F. Johnson and R. E. Rednell, Iron in Brass, Met. Ind., vol. 18, pp. 101–125; 1921.
[19] See footnote 16.

and 1.0 per cent iron had a considerably smaller grain size. The grain size of the bronze containing 1.0 per cent iron was so small that it could not be detected without the aid of the microscope. The presence of free iron in the bronze specimens was not detected under the microscope.

Representative sections of the specimens containing additions of iron are shown in Figures 7 and 8. Microscopic examination of the polished and unetched specimens (fig. 7) showed little difference in the structures of the bronzes containing 0.3 per cent or less of iron. The effect of additions of iron over 0.3 per cent was to produce segregation of the lead particles.

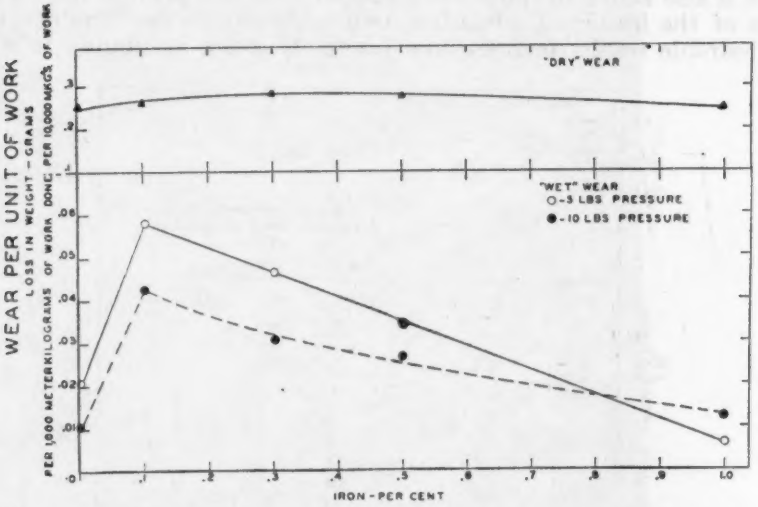

FIGURE 9.—*Effect of iron on the wear resistance of 80–10–10 bronze*

(b) RESISTANCE TO WEAR

Due to the formation of oxide films on the surfaces of bronze specimens during wear tests at elevated temperatures (350° F.), "dry" wear tests, under a test load consisting of the weight of the head of the Amsler wear-testing machine, were made at room temperature only. The upper part of Figure 9 shows additions of iron to be practically without effect on the rate of "dry" wear per unit of work done of 80–10–10 bronze.

Although the "dry" method of wear testing showed practically no difference in the rate of wear with iron additions, tests made in the presence of kerosene at reduced pressures showed rather clearly the effect of additions of iron on the rate of wear per unit of work. The lower part of Figure 9 gives the results of "wet" wear tests at loads of 5 and 10 pounds. It will be noted from this figure that the first additions of iron (up to about 0.3 per cent) increased the rate of wear markedly. Further additions of iron decreased the rate of wear steadily until at 1 per cent iron the rate of wear was practically the same as that of the iron-free bronze.

Under a load of 10 pounds the weight lost by the test specimens was actually greater than under a load of 5 pounds. The higher load, however, resulted in such an increased frictional force between the test specimens as to give smaller weight losses per unit of work than the lower load.

(c) RESISTANCE TO POUNDING

The effect of additions of iron on the resistance to pounding of 80–10–10 bronze is summarized in Figure 10.

The deformation under pounding decreased with additions of iron up to 1 per cent, this decrease being more marked in the lower range of iron content than in the higher range. Increasing the temperature of test resulted in increased deformation under pounding.

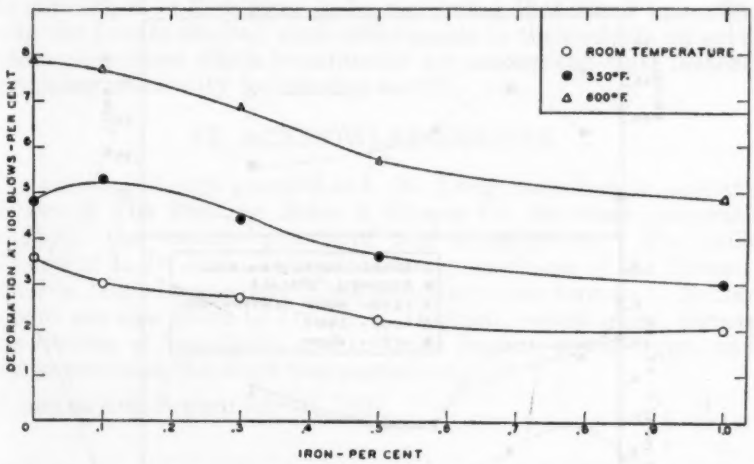

FIGURE 10.—*Effect of additions of iron on the resistance to deformation under pounding at various temperatures of 80–10–10–bronze*

(d) RESISTANCE TO SINGLE-BLOW IMPACT

The effect of additions of iron on the resistance to Izod impact is shown in the lower part of Figure 11. Increasing the iron content over 0.3 per cent decreased the notch toughness of the bronze tested at all temperatures. A test temperature of 350° F. did not materially affect the notch toughness, but the test temperature of 600° F. lowered the notch toughness markedly. Considering the resistance to impact at all test temperatures, it may be stated that additions of iron up to 0.3 per cent do not affect the notch toughness of 80–10–10 bronze.

(e) HARDNESS

Small additions of iron (up to 0.3 per cent) increase the hardness of 80–10–10 bronze. Further additions (up to 1 per cent) result in a slight decrease in the hardness, but this decrease is not great enough to offset the additional hardness gained by small additions. As shown in the upper part of Figure 11, the maximum hardness is acquired with iron additions of about 0.3 per cent.

V. SUMMARY AND CONCLUSIONS

The effect of casting temperatures (from 1,850° to 2,120° F.) and the effect of additions of iron (up to 1.0 per cent) on the wear resistance, resistance to pounding, resistance to single-blow impact, hardness, and microstructure of a bearing bronze containing 80 per cent copper, 10 per cent tin, and 10 per cent lead were studied. Many of the tests were made at 350° and 600° F. as well as at room temperature.

1. EFFECT OF CASTING TEMPERATURES

In general, an increase in the pouring temperature of the bronze from 1,850° to 2,120° F. decreased the rate of wear per unit of work;

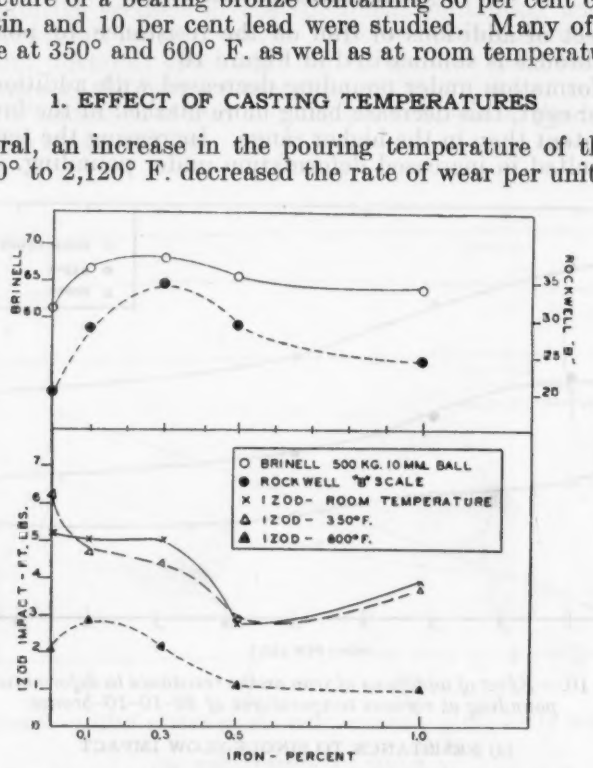

FIGURE 11.—*Effect of additions of iron on the Brinell and Rockwell hardness and Izod notch toughness values of 80–10–10 bronze*

decreased the deformation under pounding within the range of 1,850° to 1,950° F.; decreased the notch toughness of the bronzes cast close to 2,000° F.; and decreased the hardness slightly. The various temperatures of casting had very little effect on the distribution of the lead particles in the bronzes cast from 1,850° to 2,040° F. Smaller and more evenly distributed lead particles were apparent in bronzes cast at 2,120° F. An increase in the size of the grain was noted as the casting temperature increased.

It is to be kept in mind, however, that these conclusions regarding the specific effects of casting temperature on the properties of 80–10–10 bronze are strictly applicable only to sand-cast specimens and to castings of sizes or sections comparable to those employed in this experimental work.

2. EFFECT OF ADDITIONS OF IRON

The rate of wear per unit of work under "wet" tests was increased with small additions of iron. Further additions lowered the rate of wear until at 1 per cent iron the rate of wear was about the same as that of the iron-free bronze. The addition of iron up to 1 per cent decreased the deformation under pounding, this decrease becoming relatively small for additions over 0.5 per cent. Additions of iron over 0.3 per cent decreased the notch toughness. Additions of iron increased the hardness, the maximum hardness being obtained with 0.3 per cent iron. Additions of iron to the bronze caused segregation of the lead particles and considerably reduced the grain size when the iron content was over 0.3 per cent.

In general, it is therefore, to be concluded that small amounts of iron in the bronze studied were unfavorable in their effects on several of those properties which presumably are among the chief factors in determining suitability for bearing service.

VI. ACKNOWLEDGMENTS

The author is deeply grateful to L. M. Long, metallurgist, and other members of The Bunting Brass & Bronze Co. for their cooperation throughout the various phases of this investigation. The skillful assistance of L. D. Jones, senior laboratory mechanic of the Bureau of Standards, helped materially in the founding of the bronzes. Acknowlegments are also made to Dr. R. L. Dowdell, metallurgist, formerly of the Bureau of Standards, and to Louis Jordan, metallurgist, under whose supervision the work was carried on.

WASHINGTON, September 10, 1931.

RP402

ULTRASONIC MEASUREMENTS OF THE COMPRESSIBILITY OF SOLUTIONS AND OF SOLID PARTICLES IN SUSPENSION

By Chester R. Randall

Description is given of ultrasonic interferometer apparatus and a method of measuring ultrasonic velocities in liquids.

Results of ultrasonic measurements on distilled water at temperatures 0° to 86° C. and on aqueous solutions of four kinds of sugar for several concentrations and a series of temperatures are presented in curves and tables. The compressibility of distilled water and of the solutions are determined from ultrasonic velocity measurements.

Pyrex glass suspensions (aqueous) were prepared, the pyrex particles ranging in size from 2μ down. Ultrasonic velocity measurements were made on these suspensions for the purpose of testing the possibilities of a theory for getting the compressibility of a solid by a velocity-suspension method. The results obtained, though largely qualitative, show possibilities and limitations of method.

CONTENTS

		Page
I.	Introduction	79
II.	Principle of the ultrasonic interferometer	80
III.	Description of the apparatus	81
IV.	Theory for the propagation of sound in suspensions	84
V.	Preparation of suspensions	84
VI.	Measurements on pyrex glass suspensions	85
VII.	Measurements on sugar solutions	89
VIII.	Measurements on distilled water	94
IX.	Summary	99
X.	Acknowledgment	99

I. INTRODUCTION

The ultrasonic interferometer traces its origin to the first application of the piezo-electric quartz crystal in the production of ultrasonic waves in water. In 1917 Langevin [1] brought out for the detection of submarines an echo sounding device which employed as a source of sound a mosaic of quartz crystals faced with steel plates about 4 inches in diameter and 1 inch in thickness. The frequencies which he employed to drive his sounder ranged from 40 to 100 kc. This source of ultrasonic waves proved to have unexpectedly good qualities, both as to its radiating ability and to its directional characteristics.

In the year 1923, R. W. Boyle and his collaborators described in the Transactions of the Royal Society of Canada "A New Photographic Method to Demonstrate the Interference of Longitudinal Wave Trains." For his source of sound he used an ultrasonic generator built similar to that of Langevin, and depending for its action upon the piezo-electric property of quartz. Two of these

[1] Echo Sounding, Hydrographic Review (Monaco) vol. 2, No. 1, pp. 51-91; 1924-25.

sound generators were placed in a large tank of water opposite each other with their planes vertical and parallel. The same driving potential was applied to the two sound generators in phase. These sound sources were placed at such a distance apart that standing waves with vertical nodal planes were produced in the water. These standing waves were detected by fine coal cinder particles which when placed in the water settled down in the nodal planes and formed rows on a horizontal white plate placed just beneath the beam of sound. The rows formed were then photographed and from their distance apart the half wave lengths in the liquid were obtained. The precision reached in measuring the velocity of ultrasonic waves by this method was not great, about 1 per cent, but this experiment was the forerunner of many more to follow, by Boyle and by others.

Some time later, Pierce [2] developed a method for determining the velocity of ultrasonic waves in gases. There are four distinct differences between Pierce's method and that of Boyle: (1) Pierce used a single source of sound, the second source being replaced by a reflector; (2) the source of sound consisted of one single quartz crystal (in contrast with the mosaic) whose resonant frequency was determined by the dimensions of the crystal itself; (3) a critical reaction of the reflected waves on the vibrating quartz crystal indicated the existence of a system of standing waves between the source of sound and reflector; and (4) successive systems of standing waves were established by moving the reflector a half wave length closer to the source of the sound, the distance between the successive positions of the reflector determining the half wave length.

In Pierce's apparatus, the resonator crystal played the double rôle of resonator and oscillator. This system worked well for gases. Although nodal settings could be made at best to only about 0.02 mm., the accuracy in the wave length measurements for a large span of half wave lengths was very good.

A sonic interferometer for the study of liquids was later developed by Hubbard and Loomis.[3] In their apparatus, a quartz plate serving as the source of the waves was driven by an independent oscillator as in the experiments of Langevin. A system of standing waves was produced in the liquid by a reflector and the half wave length determined from the positions of the reflector for conditions of resonance. The precision obtainable in velocity measurements was found to be even greater for liquids than for gases, owing to the smaller coefficient of absorption in the case of liquids. This method for working with liquids has been extended by Hubbard [4] to the study of sound absorption in gases.

II. PRINCIPLE OF THE ULTRASONIC INTERFEROMETER

The principle of the ultrasonic interferometer depends on the setting up of a system of standing sound waves by reflection. The source of sound used by the author was a piezo-electric quartz disk (Curie cut) 7 cm in diameter and 5 mm in thickness. The schematic arrangement is shown in Figure 1. An alternating potential of high frequency is applied to the condenser plates on either side of the quartz crystal,

[2] G. W. Pierce, Proc. Am. Acad. of Arts and Sci., vol. 60, pp. 271–302; October, 1925.
[3] Hubbard and Loomis, Phil. Mag., vol. 5, pp. 1177–1190; June, 1928. Loomis and Hubbard, J. Opt. Soc. Am., and Rev. Sci. Int., vol. 17, pp. 295–307; October 1928.
[4] J. C. Hubbard, Phys. Rev., vol. 35, p. 1442; 1930; vol. 36, p. 1668; 1930.

setting up ultrasonic waves of the same frequency in the medium above. The establishment of a system of standing waves requires that the reflector shall be plane parallel with the source of the waves and an integral number of half-wave lengths away from it. Under these conditions the quartz crystal vibrates with a maximum amplitude, since the vibrations of the liquid are in resonance with those of the crystal. If the reflector is out of place this resonance is destroyed and the amplitude of the oscillating crystal is diminished. The crystal in oscillation generates a back piezo-electromotive force proportional to the amplitude of that oscillation. Accordingly, when the amplitude is a maximum the driving current is a minimum. This enables one to adjust the reflector to a nodal position. The distance between successive nodal planes is one-half of a wave length. From a measurement of these half-wave lengths and from the known frequency of

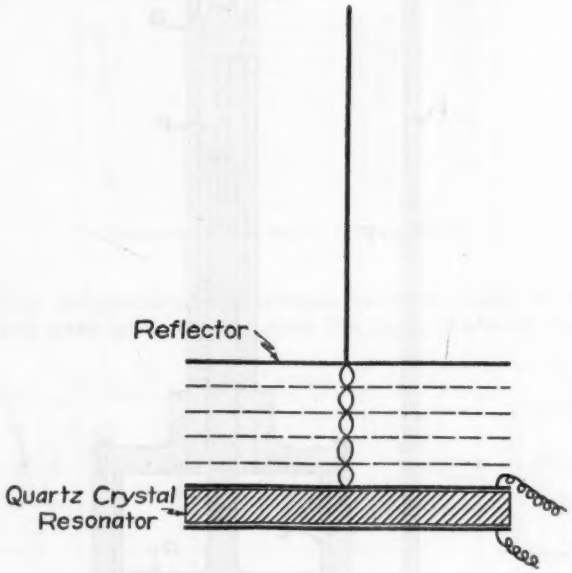

FIGURE 1.—*Principle of ultrasonic interferometer*

the alternating potential, the velocity of the ultrasonic waves may be calculated.

III. DESCRIPTION OF THE APPARATUS

A cross-section view of the interferometer itself is shown in Figure 2, which is about one-third actual size. The entire interferometer is made of metal with the exception of the quartz crystal, a bakelite cup holding the crystal, and a rubber tube insulating the alternating potential lead in. Monel metal was used practically throughout.

A cup *C* contains the liquid under investigation and the bottom of the cup, *D* (a phosphor bronze diaphragm), serves as the upper condenser plate of the quartz crystal. The sample of liquid for test may be as small as 180 cm^3. This liquid when placed in the interferometer is brought to temperature by deep immersion in a well-stirred, con-

stant temperature water bath. Water-tight seals on the outside of the interferometer at the top and bottom of the cup are secured by the use of a wax made from beeswax and rosin.

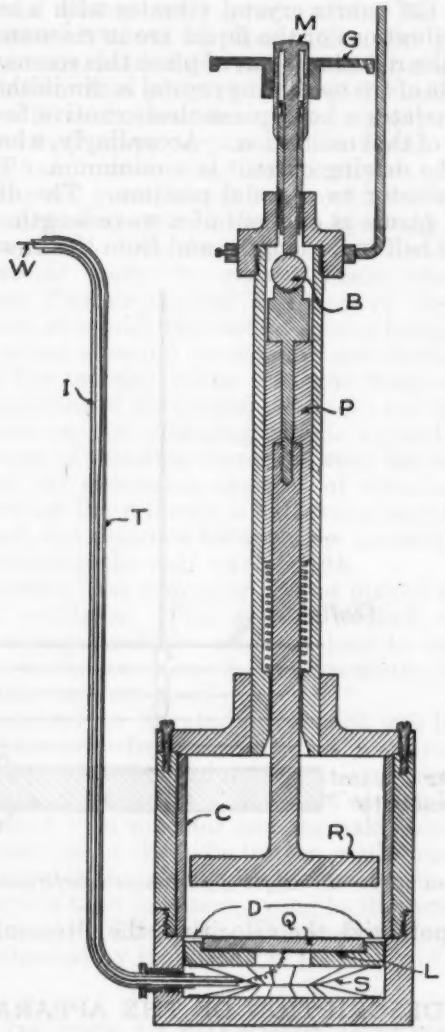

FIGURE 2.—*Ultrasonic interferometer*

R, reflector.
C, cup.
D, diaphragm.
Q, quartz crystal.
S, spring.
P, piston.
B, steel ball.
I, rubber insulation.
T, brass tube.
M, micrometer head.
W, lead wire.
G, graduated disk.
L, lower condenser plate.

Wave-length measurements are made by means of a micrometer screw, which, with the help of a spring, carries the reflector up or down and measures the distance between nodes. Upon the perfection of this screw and of its action the precision of the results is largely

dependent, and much care was taken in the selection of this important part. The screw was furnished by the Brown & Sharpe Co. It has a travel of 25 mm. This screw was tested by the gage section, of the Bureau of Standards, and was found to be accurate to 2μ.

Table 1 shows one of the sets of micrometer screw readings taken for a sugar solution and illustrates the precision obtainable. The differences in the readings give wave lengths in millimeters.

TABLE 1.—*Aqueous sucrose solution*

Sugar concentration=30.42 per cent (by weight). Temperature=30° C. Frequency=767.64 kc/sec

Node	Screw readings	Wave lengths
		mm
1	24.366	
		2.107
3	22.259	2.104
5	20.155	2.105
7	18.050	2.105
9	15.945	2.104
11	13.841	2.105
13	11.736	2.104
15	9.632	2.106
17	7.526	2.106
19	5.420	2.107
21	3.313	2.106
23	1.207	

Most probable wave length=2.1051±0.0004 mm

All possible independent differences between pairs of readings in the above set were used to calculate the most probable wave length.

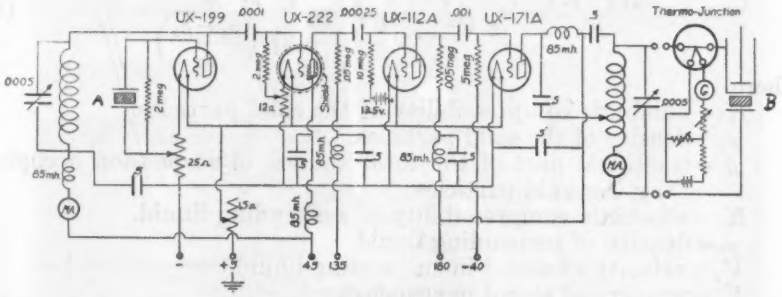

FIGURE 3.—*Constant frequency generator and amplifier used with ultrasonic interferometer*

The estimated possible error in this value was determined from measurements made six months apart on two different aqueous sucrose solutions of the above concentration and at the above temperature, the most probable value for each of four different determinations agreeing to within 0.0004 mm.

Figure 3 shows the constant frequency generator and amplifier which supplies the alternating current of ultrasonic frequency. The quartz crystal A, at the left, which controls the frequency, is driven by a small UX–199 tube with a tuned plate circuit. The resonator quartz crystal B, on the right, has a natural frequency of 550 kc., but is driven at the frequency of the control crystal, about 750 kc.

Other control frequencies ranging from 200 to 750 kc have been used, but the high frequency was preferable on account of a somewhat increased regularity of nodes for shorter wave lengths. Changes in the current driving the crystal resonator were observed by means of a hot wire-thermocouple unit used in conjunction with a reflecting galvanometer.

A photograph of the assembled apparatus (fig. 4) shows from left to right the constant temperature crystal chamber, the oscillator and amplifier, the water bath of 30 liters capacity, and the interferometer immersed in the water. The temperature of the water in the bath is maintained constant to $\pm 0.02°$C. and uniform throughout by means of a heating coil and rotating propeller located in a tube open at its ends near the top and bottom of the bath. The change in temperature of the liquid in the interferometer could be followed by observing the change in the wave length. Constancy of temperature was usually reached in one hour.

IV. THEORY FOR THE PROPAGATION OF SOUND IN SUSPENSIONS

Professor Herzfeld,[5] of the Johns Hopkins University has recently developed a theory for the "propagation of sound in suspensions," and has suggested the possibility of determining the compressibility of solids by making measurements of the velocity of ultrasonic waves first in the suspension and then in the suspending liquid with the solid particles removed by filtration or settling. The compressibility relation is formulated as follows:

$$\frac{K_1-K_2}{K_2}=\frac{V^2{}_2-V^2}{\beta V^2}-\frac{V^2{}_2}{V^2}\frac{\left(\frac{\rho_1-\rho_2}{\rho_2}\right)}{1+\frac{1}{3}\beta\left(\frac{\rho_1-\rho_2}{\rho_2}\right)} \tag{1}$$

where

K_1 = adiabatic compressibility of the solid particles.
ρ_1 = density of the solid particles.
β = fractional part of the total volume of suspension occupied by the solid particles.
K_2 = adiabatic compressibility of suspending liquid.
ρ_2 = density of suspending liquid.
V_2 = velocity of sound in suspending liquid.
V = velocity of sound in suspension.

Formula (1) involves several assumptions—that the particles are small compared to the wave length, that the amplitude of the waves is small compared to the wave length, that the damping of the waves is negligible, and that the accompanying transversal waves are negligible.

V. PREPARATION OF SUSPENSIONS

The preparation of suitable suspensions is a matter of much difficulty. The conditions to be satisfied are: (1) The solid particles should be small enough to remain in suspension for about two hours with the help of only a moderate amount of stirring, (2) the particles

[5] K. F. Herzfeld, Phil. Mag., vol. 9, No. 59, supplement, pp. 741–751, 752–768; May, 1930. On p. 768 there appears a formula (59) which corresponds to formula (1) above. An error appearing in formula (59) has been corrected in formula (1).

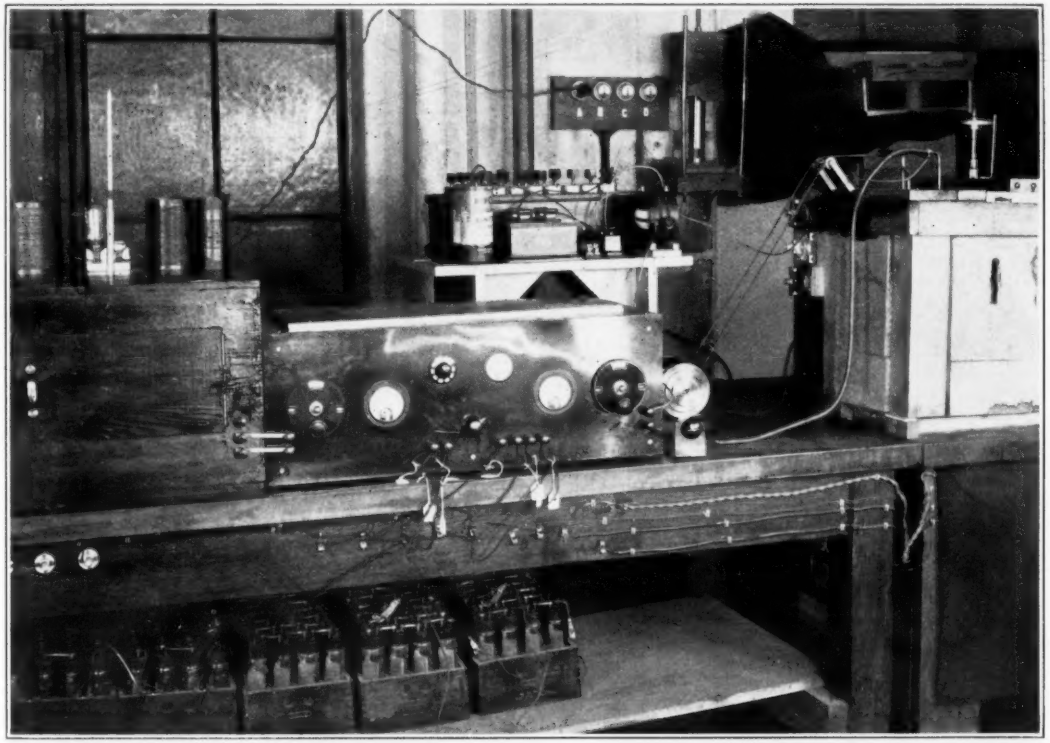

FIGURE 4.—*Ultrasonic interferometer apparatus*

UNIV. OF MICH.

must take up a uniform distribution throughout the liquid, (3) the compressibility ratio of solid to suspending liquid should be large as should also the volume concentration of the solid in suspension in order to determine the compressibility of the particles with only a few per cent of error, and (4) the solid material chosen for the experiment should be one for which the compressibility has been determined by direct pressure measurements in order that a check of the theory may be possible.

Sodium chloride was the first solid to be tried. The suspending liquid adopted was a mixture of bromoform ($CHBr_3$) and tetrachlorethane ($C_2H_2Cl_4$) in such proportions as to produce a liquid of the density of NaCl, 2.160 at 30° C. The NaCl was fused in a platinum crucible and ground with a mortar and pestle. Only those particles which would pass a 200-mesh sieve were chosen for the suspension. As it happened, the labor of pulverizing and sifting the material was entirely lost, for as soon as the fine particles were placed in the liquid they began to cluster in cloud-like masses.

Xylene was tried as a suspending liquid, but while the particles did not seem to cluster so extensively, they could not be made fine enough to remain suspended for more than two or three minutes. Out of 500g of ground material, the amount of NaCl which was fine enough to remain in suspension gave a concentration of only 0.005 per cent.

Zinc oxide particles, all of which were below 1μ in diameter, were tried both in water and in xylene, but the particles showed a tendency to stick together and dropped out of suspension very rapidly.

It was recognized that this tendency to flocculate might be due to traces of water in the liquid or in the salt particles, and special attention was given to this possibility. The liquids were dehydrated as completely as possible, both by partial freezing and by distillation and the salt particles were dried in a current of warm air that had passed through a dehydrating tower, but no appreciable diminution in the flocculation was perceptible.

It was recognized also that electrification might be causing the trouble, and the use of radium compounds in the neighborhood of the particles was resorted to, but without appreciable improvement.

VI. MEASUREMENTS ON PYREX GLASS SUSPENSIONS

The only satisfactory suspensions prepared were those of powdered laboratory pyrex glass in distilled water (containing a very small amount of HCl). Pyrex rod was ground in a steel ball mill for 48 hours. The pyrex was then found to be flour fine. It was placed in a pyrex jar and treated with a 50 per cent HCl solution to remove the iron impurity introduced in grinding. After diluting the acid and allowing the pyrex particles to settle for two days, the acid solution was siphoned off and discarded. Distilled water was then added to the pyrex residue left in the jar and the residue brought into suspension by stirring. After 24 hours' settling, the liquid containing the particles still in suspension was siphoned off and saved. This process of adding water, stirring, settling, and siphoning was repeated many times until over 20 liters of fine suspension had been obtained. A sample of the suspension was examined under a high-power microscope and all the particles were found to be smaller than 2μ in diameter, with no tendency to cling together.

The volume concentration of the solution as obtained was about 0.25 per cent. As this was too small to be suitable for measurements, the suspension was concentrated by evaporation. Two different concentrations were used in the experiments, of strengths 5 and 15 per cent by weight. To insure that the particles did not settle out of suspension during the measurements, the reflector was lowered and raised through its full travel every five minutes while the liquid was being brought to constant temperature. In addition, the reflector was similarly moved just before each reading of the nodal position. Had there been any appreciable settling of the suspended particles during the measurements it would have produced a difference of wave length in the upper and lower levels of the liquid. No such effect was noticed.

The sharpness of the nodes in the system of standing waves was considerably reduced when the particles were present in the suspending liquid. However, the wave length could be determined with a maximum error of 0.04 per cent. For both suspensions, there was a decrease in velocity when the particles were present in the liquid, the more concentrated suspension showing a decrease in velocity of 0.4 per cent. The wave lengths in the suspensions had been determined from the positions of the reflector for minimum driving current. There was, however, considerable damping of the waves which produced a gradual broadening of the pattern of maxima and minima, so that the velocity as calculated from the minima is too large. Calculating from the minima alone, the decrease of velocity in the suspensions is less than half that required by the theory. Substituted in equation (1) this decrease in velocity leads to a negative compressibility for the pyrex particles as shown in Table 2.

TABLE 2

β Pyrex concentration (by volume)	ρ_2 Density of suspending liquid	ρ_1 Density of pyrex particles	V Velocity in suspension	V_2 Velocity in suspending liquid	K_1/K_2 Compressibility of pyrex particles / Compressibility of suspending liquid
0.0222	0.999	2.23$_0$	1,511.$_0$	1,513.$_0$	−0.10
.0718	.999	2.23$_0$	1,506.$_1$	1,513.$_0$	−.08

The density ρ_1 for the laboratory pyrex glass of the particular lot worked with was determined both for the pyrex rod and the pyrex powder. The density of the rod was obtained from its weight in air and its loss of weight in distilled water; the density of the powder was found by means of a specific gravity bottle using distilled water as the wetting liquid. Both methods gave the same result, the value being 2.230 g/ml.

The volume concentration β for each suspension was determined as follows:

$$\beta = \frac{M_1/\rho_1}{\frac{M - M_1}{\rho_2} + \frac{M_1}{\rho_1}}$$

where

M = mass of suspension.
M_1 = mass of pyrex particles.
ρ_1 = density of pyrex particles.
ρ_2 = density of suspending liquid.

Negative values for the compressibility are, of course, impossible. The broadening effect due to damping seemed to be of sufficient

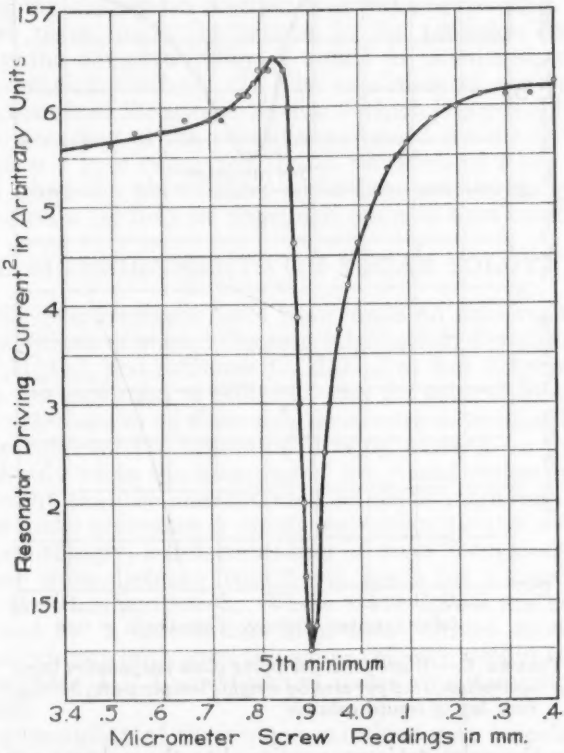

FIGURE 5.—*Wave form for pyrex glass suspension (concentration, 18.2 per cent by weight; temperature, 30° C.), near bottom of liquid column*

magnitude to account for the negative results obtained. It will be remembered that in the development of formula (1) one of the assumptions made was that the damping was negligible. To see if this were the case, a study of the interference pattern was undertaken, complete curves for the galvanometer readings being taken at distances 4 and 24 mm from the source, the suspension being 18.2 per cent by weight of pyrex glass in water. These curves are shown in Figures 5 and 6.

To a first approximation the point on the steep part of the curve in Figure 5 cut by a straight line joining the level parts of the curve may be taken as homologous with the corresponding point on the curve in Figure 6. The difference between the velocity as determined from these two points and the velocity determined from the minima is found to be 6.9 $\frac{\text{meters}}{\text{second}}$. This velocity correction applies to a volume concentration of 9.1 per cent pyrex. Assuming that this damping

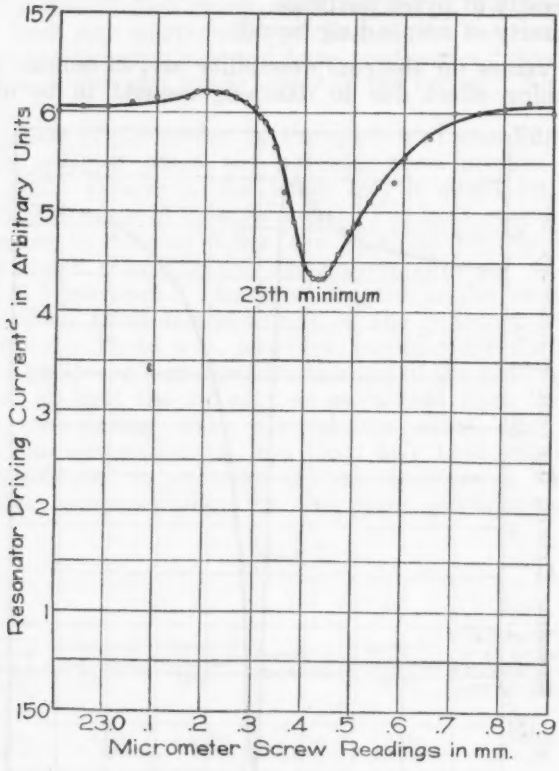

FIGURE 6.—*Wave form for pyrex glass suspension (concentration, 18.2 per cent by weight; temperature, 30° C.), near top of liquid column*

correction to the velocity is proportional to the volume concentration, values are obtained as shown in Table 3 below.

TABLE 3

β Pyrex concentration (by volume)	ρ_2 Density of suspending liquid	ρ_1 Density of pyrex particles	V Velocity in suspension	V_2 Velocity in suspending liquid	K_1/K_2 Compressibility of pyrex particles / Compressibility of suspending liquid
0.0222	0.999	2.23_0	1,509.3	1,513.0	−0.006
.0718	.999	2.23_0	1,500.7	1,513.0	+.013

The precision to be obtained in determining the compressibility of a solid in powdered form by the suspension method is not great. In the present experiment it may be seen that a variation in V of 1 part in 3,000 will alter the value of K_1/K_2 in Table 3 by 0.03 at the lower concentration ($\beta=0.0222$), and by 0.01 at the higher concentration ($\beta=0.0718$). Taking into account the calculated errors the compressibility ratios found for the two concentrations agree well within those limits.

The compressibility of pyrex glass has been determined from direct pressure measurements by Bridgman[6] and by Adams and Gibson[7], the assigned value in both investigations being 3.1×10^{-6} atm. $^{-1}$ at atmospheric pressure. This would give for K_1/K_2 the value 0.07. The difference between this value and the maximum value assignable as found by the suspension method is as yet unexplained.

There are three major limitations in the precision attainable in determining the compressibility of solids in powdered form by the velocity-suspension method: (1) The smallness of the ratio K_1/K_2, (2) the magnitude of the concentration β which it is possible to obtain, and (3) the accuracy of the velocities obtained for the liquid and for the suspension. It is estimated that a precision of 1 per cent might be reached when the above three conditions are the most favorable, provided formula (1) may be depended upon to that extent.

VII. MEASUREMENTS ON SUGAR SOLUTIONS

Ultrasonic measurements have been made on aqueous solutions of four different kinds of sugar: Sucrose ($C_{12}H_{22}O_{11}$), dextrose ($C_6H_{12}O_6$), levulose ($C_6H_{12}O_6$), and raffinose ($C_{18}H_{32}O_{16}$) at five different temperatures (with the exception of raffinose) and for several concentrations. The sound velocities in all these solutions were determined from positions of the reflector for minimum driving current—a procedure to be followed only when the damping of the sound waves is negligible. It was thought that the concentrated solutions might show sufficient damping to make necessary a small correction to the velocities obtained. Accordingly, a determination of wave form near the source of sound and some distance from it was made for a sucrose solution of 30.4 per cent concentration. These wave forms are compared in Figures 7 and 8. A calculation from these curves shows that the maxima and minima both give the same velocity within the accuracy of the measurements. Consequently, there is no damping correction to be applied.

The compressibility of these sugar solutions may be calculated just as for any liquid from sound velocity and density measurements by the following well-known relation due to Laplace

$$V=\sqrt{\frac{1}{\beta_\phi \rho}} \tag{4}$$

where

V = velocity of sound.
β_ϕ = adiabatic compressibility.
ρ = density.

[6] P. W. Bridgman, Am. J. Sci., vol. 10, p. 363; 1925.
[7] Adams and Gibson, J. Washington Acad. Sci., vol. 21, p. 384; 1931.

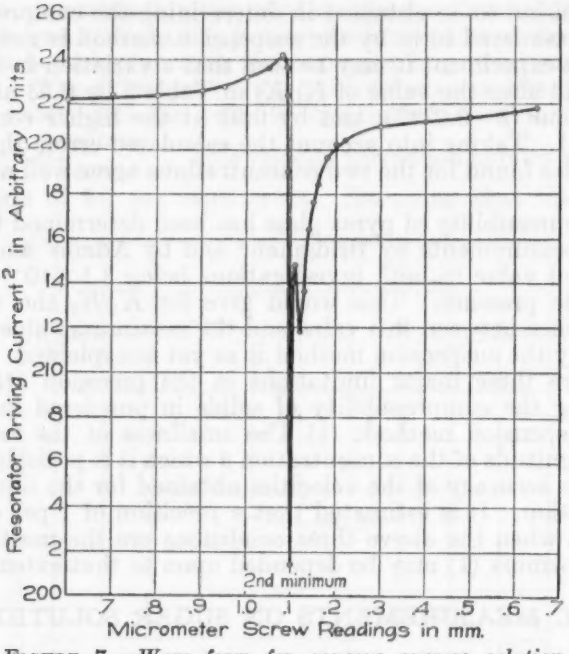

FIGURE 7.—*Wave form for aqueous sucrose solution (concentration, 30.4 per cent by weight; temperature, 30° C.), near bottom of liquid column*

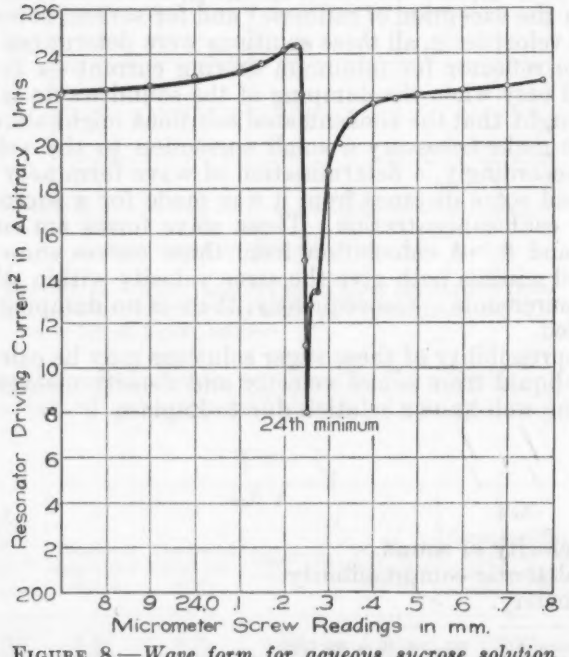

FIGURE 8.—*Wave form for aqueous sucrose solution (concentration, 30.4 per cent by weight; temperature, 30° C.), near top of liquid column*

Values of the compressibility thus obtained are shown in Tables 4 and 5. For the sucrose solutions the values of ρ were taken from Plato's tables. The values of ρ for the other solutions were determined experimentally.

TABLE 4.—*Compressibility (adiabatic) of aqueous sugar solutions at 30° C. for different concentrations*

SUCROSE ($C_{12}H_{22}O_{11}$)

Concentration	Density	Velocity	Compressibility $\times 10^6$
g sugar / 100 g solution	*g / ml*	*meters / sec.*	*atm.$^{-1}$*
0	0.9957	1,509.9	44.62
.87	.9990	1,512.3	44.34
3.95	1.0111	1,520.1	43.34
7.88	1.0267	1,531.4	42.08
11.91	1.0432	1,543.6	40.76
20.13	1.0783	1,572.3	38.01
30.42	1.1252	1,615.8	34.49

RAFFINOSE ($C_{18}H_{32}O_{16}$)

4.07	1.0117	1,520.8	43.31
9.15	1.0326	1,535.8	41.60
17.30	1.0677	1,563.3	38.84
27.01	1.1124	1,603.4	35.42

DEXTROSE ($C_6H_{12}O_6$)

2.11	1.0039	1,516.9	43.80
9.62	1.0334	1,544.8	41.10
18.74	1.0712	1,583.0	37.74
35.27	1,1457	1,670.0	31.71

LEVULOSE ($C_6H_{12}O_6$)

1.96	1.0033	1,516.8	43.91
5.96	1.0192	1,531.8	42.30
11.79	1.0428	1,554.7	40.10
17.47	1.0668	1,579.8	38.06

TABLE 5.—*Compressibility (adiabatic) of aqueous sugar solutions at different temperatures*

SUCROSE SOLUTION—PER CENT SUGAR=11.91

Temperature	Density	Velocity	Compressibility $\times 10^6$
° C.	*g / ml*	*meters / sec.*	*atm.$^{-1}$*
0	1.0496	1,448.8	46.03
10	1.0482	1,488.8	43.61
20	1.0461	1,520.8	41.93
30	1.0432	1,543.6	40.76
40	1.0395	1,560.7	40.01

SUCROSE SOLUTION—PER CENT SUGAR=30.42

0	1.1348	1,544.8	37.42
10	1.1322	1,575.8	36.04
20	1.1290	1,599.3	35.09
30	1.1252	1,615.8	34.49
40	1.1208	1,627.2	34.14

TABLE 5.—*Compressibility (adiabatic) of aqueous sugar solutions at different temperatures*—Continued

DEXTROSE SOLUTION—PER CENT SUGAR=18.74

Temperature	Density	Velocity	Compressibility $\times 10^6$
° C.	$\frac{g}{ml}$	$\frac{meters}{sec.}$	$atm.^{-1}$
0	1.0790	1,499.7	41.7
10	1.0772	1,535.2	39.9
20	1.0747	1,562.5	38.6
30	1.0712	1,583.0	37.7
40	1.0670	1,597.1	37.2

LEVULOSE SOLUTION—PER CENT SUGAR=17.47

0	1.0756	1,500.4	41.8
10	1.0735	1,534.9	40.0
20	1.0706	1,560.9	38.8
30	1.0668	1,579.3	38.0
40	1.0623	1,592.7	37.6

Figures 9, 10, 11, and 12 below show the results of Tables 4 and 5 in the form of graphs. In Figure 9 it may be noticed that the velocity

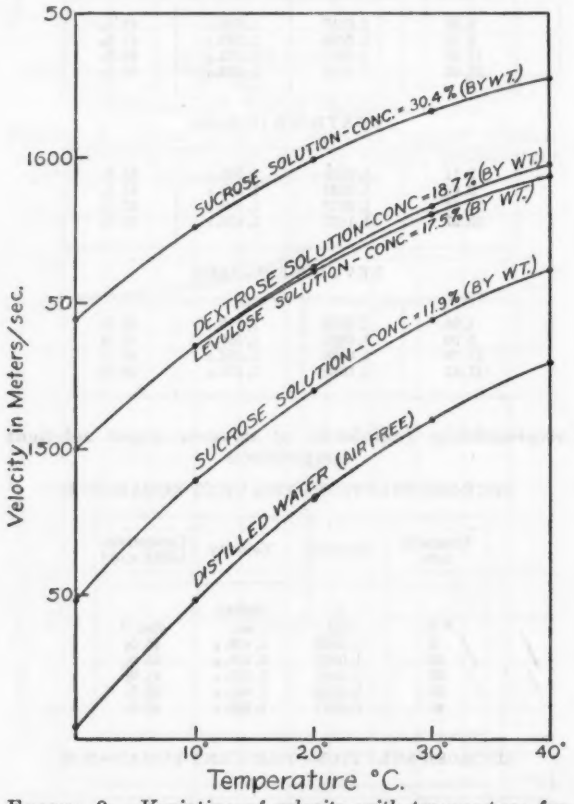

FIGURE 9.—*Variation of velocity with temperature for aqueous sugar solutions*

curves for the dextrose and levulose solutions start out together at low temperatures but gradually separate as the temperature rises.

This is remarkable in view of the fact that both sugars have the same chemical formula, differing only as optical isomerides. Figure 10 shows the same result occurring for increasing concentration; with the curves for raffinose and sucrose also similarly associated. It will be noted that the solutions of dextrose and levulose, with molecular

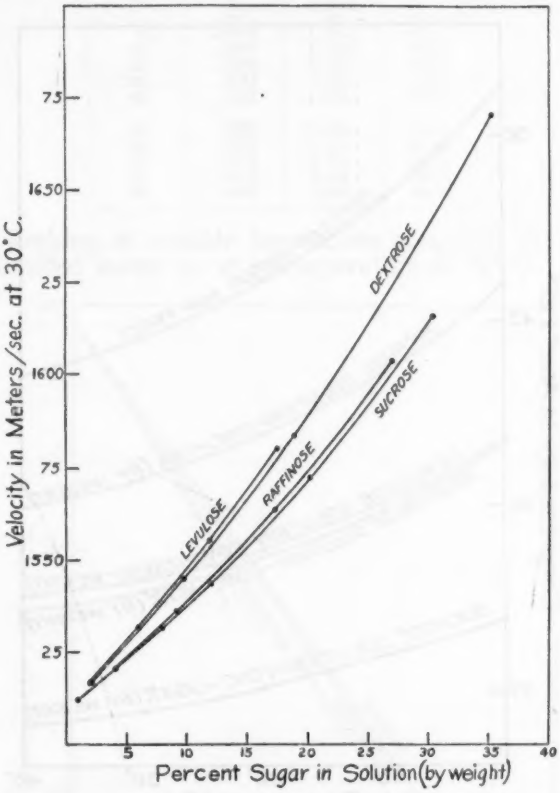

FIGURE 10.—*Variation of velocity with concentration for aqueous sugar solutions*

weights less than that of sucrose, exhibit higher velocities than sucrose, but the solutions of raffinose, which has a much greater molecular weight than sucrose, do not exhibit lower, but slightly greater velocities. Figure 12 shows that the compressibility of sugar solutions varies almost linearly with the concentration. The curves are very slightly concave downward.

VIII. MEASUREMENTS ON DISTILLED WATER

Measurements have been made on distilled water over a temperature range from 0° to 86° C. The water was first boiled in a pyrex flask to eliminate dissolved air. The velocity of ultrasonic waves in water and the adiabatic compressibility of water for the above

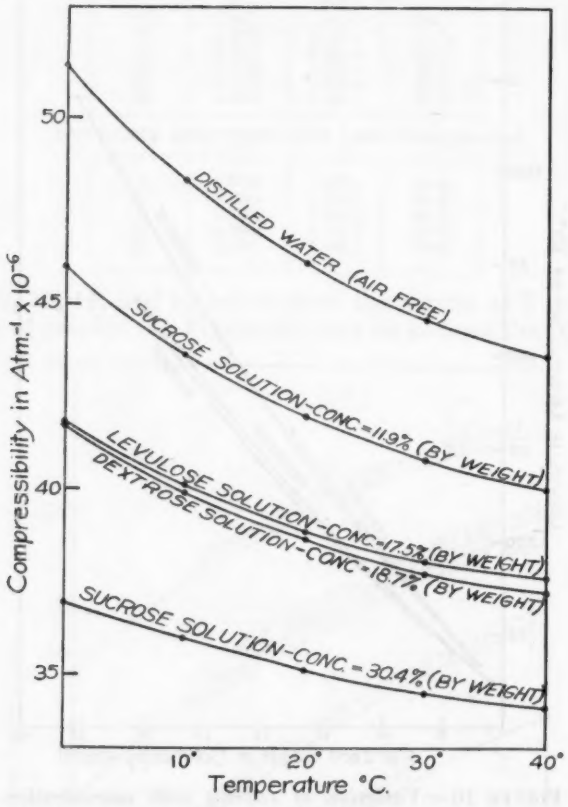

FIGURE 11.—*Variation of adiabatic compressibility with temperature for aqueous sugar solutions*

temperature range are given in Table 6 and represented graphically in the two curves of Figure 13. The upper curve shows that the velocity increases the most rapidly at 0° C., reaches a maximum at about 74° C., and then diminishes. The lower curve shows that the compressibility likewise changes the most rapidly at 0° C., with a minimum appearing at about 64° C.

TABLE 6.—*Compressibility (adiabatic) of distilled water (air free) at different temperatures*

Temperature	Density	Velocity	Compressibility $\times 10^6$
° C.	$\frac{g}{ml}$	$\frac{meters}{sec.}$	$Atm.^{-1}$
0	0.9999	1,403.5	51.4
10	.9997	1,448.0	48.3
20	.9982	1,483.1	46.1
30	.9957	1,509.0	44.6
40	.9922	1,529.5	43.6
50	.9881	1,543.5	43.0
60	.9832	1,551.5	42.8
70	.9778	1,555.3	42.8
80	.9718	1,554.6	43.1
86	.9680	1,552.4	43.4

Pooler [8] working at audible frequencies measured the velocity of sound in distilled water up to a temperature of 70° C. Though he

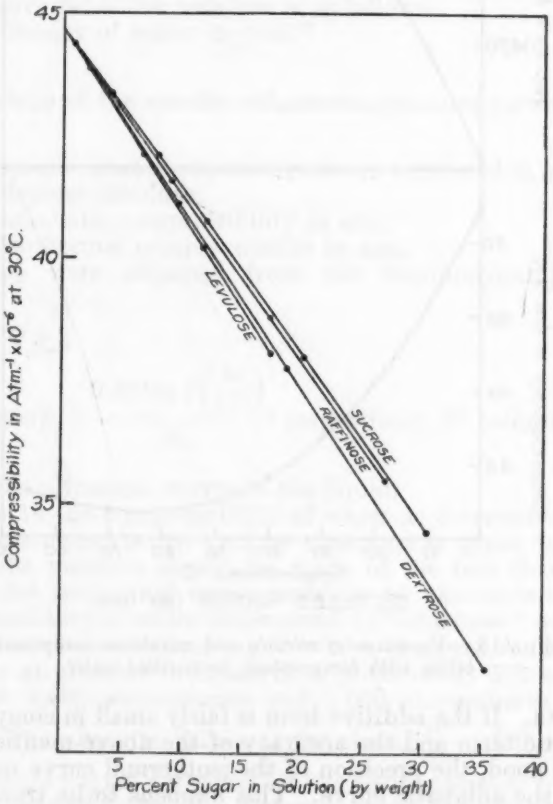

FIGURE 12.—*Variation of adiabatic compressibility with concentration for aqueous sugar solutions*

did not reach the temperature for a maximum velocity he did find a minimum compressibility which occurred at about 63° C., practi-

[8] L. G. Pooler, Phys. Rev., vol. 35, pp. 832-847; April, 1930.

cally coinciding with that found at ultrasonic frequencies. By direct pressure measurements Tyrer [9] likewise found a minimum, though at a somewhat higher temperature.

The isothermal compressibility curve for a liquid must lie above the adiabatic curve, but does not necessarily run parallel to it. This curve may be obtained from the adiabatic values plus an additive term determined from specific heat at constant pressure and specific

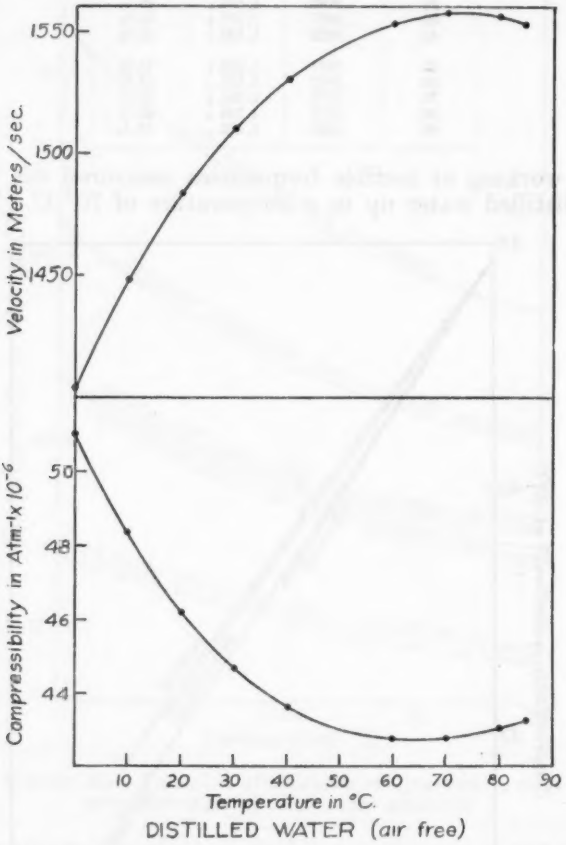

FIG. 13.—*Variation of velocity and adiabatic compressibility with temperature fordistilled water.*

volume data. If the additive term is fairly small in comparison with the adiabatic term and the accuracy of the above-mentioned data is reasonably good, the precision of the isothermal curve may be equal to that of the adiabatic curve. This happens to be true in the case of water. Accordingly Table 7 has been prepared and the results shown graphically in Figure 14.

[9] D. Tyrer, J. Chem. Soc., vol. 103, p. 1687; 1913.

TABLE 7.—*Compressibility (isothermal) of distilled water (air free) at different temperatures*

Temperature	ρ	$\left(\frac{\delta v}{\delta T}\right)_p \times 10^6$	C_p	$\frac{0.1013\rho T\left(\frac{\delta v}{\delta T}\right)_p^2}{C_p} \times 10^6$	$\beta_\phi \times 10^6$	$\beta_T \times 10^6$
° C.						
0	0.9999	−68	4.22	0.03	51.4$_4$	51.4$_7$
10	.9997	+88	4.19	.05	48.3$_4$	48.3$_9$
20	.9982	207	4.18	.30	46.1$_4$	46.4$_4$
30	.9957	304	4.17	.68	44.6$_8$	45.3$_1$
40	.9922	387	4.18	1.13	43.6$_8$	44.7$_8$
50	.9881	462	4.18	1.65	43.0$_4$	44.6$_9$
60	.9832	532	4.18	2.24	42.8$_1$	45.0$_5$
70	.9778	597	4.18	2.90	42.8$_4$	45.7$_4$
80	.9718	661	4.19	3.63	43.1$_4$	46.7$_7$
86	.9680	698	4.19	4.10	43.4$_4$	47.5$_4$

In the above table the notation is as follows:

ρ = density of water in g/ml.[10]

$\left(\frac{\delta v}{\delta T}\right)_p$ = slope of the specific volume-temperature curve.[10]

C_p = specific heat at constant pressure expressed in joules/g° C.[10]

T = degrees absolute.

β_ϕ = adiabatic compressibility in atm.$^{-1}$.

β_T = isothermal compressibility in atm.$^{-1}$.

β_ϕ and β_T were obtained from the thermodynamic relations

$$V = \sqrt{\frac{1}{\beta_\phi \rho}}$$

and $\beta_T = \beta_\phi + \dfrac{0.1013\rho T\left(\frac{\delta v}{\delta T}\right)_p^2}{C_p}$ respectively, V being the velocity of the ultrasonic waves in the liquid.

In Figure 14 the compressibility of water as determined by direct pressure measurements by various observers is given for comparison. Specific mention should be made of the fact that the curve represents the isothermal compressibility at atmospheric pressure. The compressibility of water determined by Bridgman [11] was obtained from specific volume measurement over a pressure range of 12,000 atmospheres at pressure intervals of approximately 500 atmospheres for the first 2,000 atmospheres and 1,000 atmospheres for higher pressures. The absolute values of the slope, $\frac{dv}{dp}$, of the isothermal volume-pressure curves are given for the entire range of pressure and for temperatures 0° to 80° C. For pressures 0 to 2,000 atmospheres, the slopes are given at 500 atmosphere intervals. Considering the rapid change of slope over this part of the range, the compressibility values found from the curves at the origin and those found from velocity measurements agree for the most part remarkably well. Tyrer made

[10] Values obtained from International Critical Tables.

[11] P. W. Bridgman, Proc. Am. Acad. Arts and Sci., vol. 47, pp. 441–558, 1912; vol. 48, pp. 309–362; 1912.

direct adiabatic pressure measurements working between the pressure limits 1 and 2 atmospheres and gives compressibility values which should be identical with the compressibility at atmospheric pressure. His values for compressibility are consistently slightly smaller than those determined from velocity measurements.

Recently direct pressure measurements were made by Jessup[12] for pressure limits 0 to 50 atmospheres by steps of 10. Within the accu-

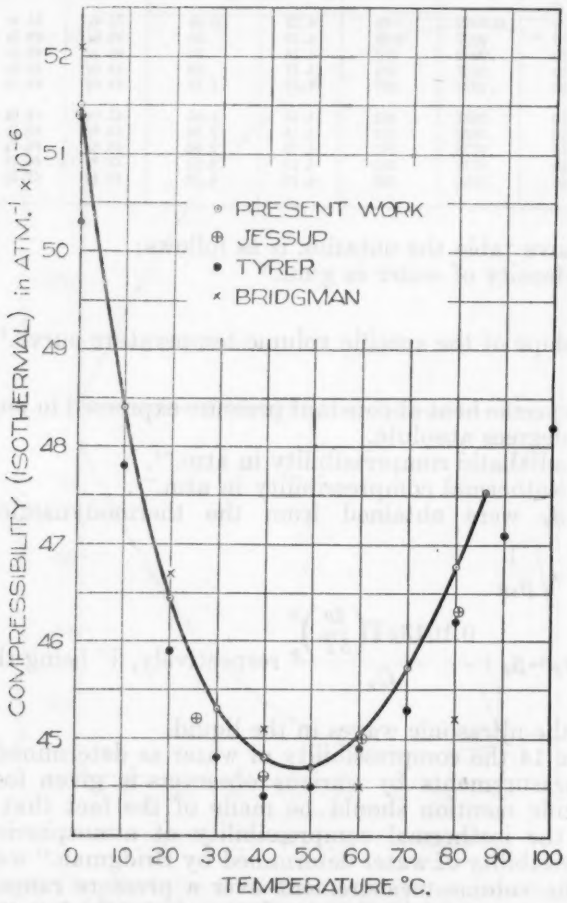

FIGURE 14.—*Isothermal compressibility of distilled water determined from velocity measurements at atmospheric pressure compared with results of direct pressure measurements*

racy attainable from the 10 atmospheres pressure changes no measurable variation in compressibility with pressure over the range 0 to 50 atmospheres was found. Consequently the values which he gives represent compressibilities for pressure limits 0 and 50 atmospheres. At the two temperatures, 0° and 60° C. his values fall almost exactly on the curve determined from velocity measurements, the remaining four points falling below the curve. In all cases his

[12] R. S. Jessup, B. S. Jour. Research, vol. 5; November, 1930.

results of direct pressure measurements and the present results determined from velocity measurements differ by not more than 1 per cent. This difference may be explained from the results of Bridgman, who worked at the much higher pressures. Bridgman found the compressibility of water at 500 atmospheres to be from 12 to 15 per cent lower than that at atmospheric pressure. Accordingly, the compressibility of water determined from volume differences for pressures 0 and 50 atmospheres might be low for a point at the origin (atmospheric pressure) by 0.6 per cent. The difference between the results of Jessup and those of ultrasonic velocity measurements are thus mainly due to the limitations set by the two different conditions of experiment

IX. SUMMARY

A description is given of ultrasonic interferometer apparatus for measuring ultrasonic velocities in liquids.

Velocity measurements on aqueous solutions of sucrose, raffinose, dextrose, and levulose (and density determinations on the three latter) have been made for concentrations 0 to 30, 27, 35, and 17 per cent, respectively, and for a temperature range 0° to 40° C. The velocities and compressibilities (adiabatic) of the solutions are presented in curves and tables.

Velocity measurements were made on distilled water (air free) covering a temperature range 0° to 86° C. A table of values and curve show the variation of velocity and compressibility (adiabatic and isothermal) with temperature.

Pyrex-glass suspensions in distilled water (containing a very small amount of HCl) were prepared, the diameter of the pyrex particles ranging from 2μ down. Concentrations of 5 and 15 per cent were used for velocity measurements. The velocity decreased as the concentration increased, the decrease in velocity, as determined by minima being 0.4 per cent for the 15 per cent concentration. The change in velocity thus determined, though in the right direction, was less than half that predicted by theory. In these suspensions, however, the waves are strongly damped, the minima being shifted so as to give an apparent velocity which is too large. A correction applied for the damping yields values for the velocity more nearly in accord with those demanded by theory.

X. ACKNOWLEDGMENT

The author wishes to express his appreciation to Dr. J. C. Hubbard for his assistance in the development of the apparatus used in making the measurements on liquids and suspensions; to Dr. K. F. Herzfeld, who developed the theory for solids in suspension with the idea of making possible measurements of the compressibility of solids by the use of the ultrasonic interferometer; and to both for their kindly aid and advice during the many months of experimental work.

The friendly cooperation of the staff of the Bureau of Standards has helped materially in carrying out this research. Especially does the author wish to thank Dr. Paul R. Heyl for his helpful suggestions from time to time and his kindly interest in the work in general.

WASHINGTON, November 11, 1931.

ON ELIMINATION OF LIQUID CONTACT POTENTIALS WITH POTASSIUM CHLORIDE AND AMMONIUM CHLORIDE

By G. M. Kline, M. R. Meacham, and S. F. Acree

ABSTRACT

The method of employing 4.1 *N* potassium-chloride solution for annulling contact potentials between hydrochloric-acid and potassium-chloride solutions gives results within the present routine experimental errors and uncertainties regarding the contact potentials. The Bjerrum extrapolation correction is over three times as large as it should be, especially if used outside the limit of about 2 mv set by him. The use of the so-called "saturated" 3.5 *N* instead of the 4.1 *N* potassium-chloride solution may often leave an error of 1 to 3 mv, or more. In view of (1) the approximately correct, experimentally verified results given by the Loomis-Acree method, (2) its simplicity and rapidity, and (3) the avoidance of uncertain extrapolations, its adoption for general use is recommended for annulling contact potentials between (*a*) hydrochloric acid and especially organic salts and buffers on the one hand and (*b*) potassium-chloride or sodium-acid phthalate solutions used in standard or reference electrodes. An approximately isoelectric eliminator, such as 3 N KCl+N KNO_3 should be used between solutions with pH values between 3 and 10.

CONTENTS

		Page
I.	Introduction	101
II.	Extrapolation method for correcting for contact potential	102
III.	Elimination of contact potential with saturated potassium chloride	103
IV.	Comparison of these methods with the system HgCl-0.1 *N* KCl-x KCl-0.1 N HCl-H_2-Pt	104
V.	Elimination of contact potentials of organic acids and acid salts	106
VI.	Discussion of standardization on one method of eliminating contact potential	109
VII.	Summary	110

I. INTRODUCTION

Contact potential is the source of greatest uncertainty, other than the purity of the water,[1] in comparative studies of the electrometric and isohydric colorimetric methods for measuring accurately the concentration or activity of hydrogen and other ions, and salt effects.[2] Such a potential is set up when the liquid of a standard reference electrode is brought into contact with complex solutions of xylans and lignins from cornstalk and other cellulosic wastes, and with paper,[3] pulp, soils,[4] tannin,[5] and other extracts, especially when very acid[6]

[1] Fawcett, E. H., and Acree, S. F., The Problem of Dilution in Colorimetric H-ion Measurements. I. Isohydric Indicator Methods for Accurate Determination of pH in Very Dilute Solutions, J. Bact., vol. 17, p. 168; 1929. Isohydric Indicators and Superpure Water, Ind. Eng. Chem., Anal. ed., vol. 2, p. 78; 1930. Aeration of Buffers, B. S. Jour. Research, vol. 6, p. 757; 1931.

[2] Acree, S. F., and Fawcett, E. H., The Problem of Dilution in Colorimetric H-ion Measurements, Ind. Eng. Chem., Anal. ed., vol. 2, p. 78; 1930.

[3] Shaw, M. B., Hydrogen Ion Concentration in the Paper Mill, Paper Trade J., vol. 81, p. 59; 1929.

[4] Snyder, E. F., Methods for Determining the Hydrogen Ion Concentration of Soils, Circular No. 56, U. S. Dept. of Agriculture; 1928. The Application of the Antimony Electrode to the Determination of the pH Values of Soils, Soil Science, vol. 26, p. 107; 1928.

[5] Wallace, E. L., and Beek, J., A Comparison of the Quinhydrone and Hydrogen Electrodes in Solutions Containing Tannin. B. S. Jour. Research, vol. 4, p. 737; 1930.

[6] Blum, W. C., and Bekkedahl, N., The Measurement of pH in Nickel Plating Solutions, Trans. Am. Electrochem. Soc., vol. 56, p. 287; 1929.

or alkaline. This liquid junction potential or contact potential may easily vary from 5 to 35 or more millivolts and failure to account for it properly may cause errors of tenths of pH units.

Formulas devised by Nernst,[7] Planck,[8] Negbaur,[9] Johnson,[10] Henderson,[11] Cumming,[12] Lewis,[13] and especially the recent important developments by MacInnes[14] and his students, and E. R. Smith[15] for calculating the contact potential can be applied at present only in comparatively simple cases. The one absolute method of measuring simultaneously contact potentials and electrode potentials devised by MacInnes and the three by Acree[16] are limited in application. The only general method available is that of approximate elimination of the contact potential.

II. EXTRAPOLATION METHOD FOR CORRECTING FOR CONTACT POTENTIAL

Tower[17] used several concentrations ($N/128$ to $N/1$) of potassium chloride and of potassium nitrate and other salts in the study of the elimination of contact potentials. As the highest concentration of the potassium chloride was $N/1$ and the experimental error of their time was 2 to 3 mv, the magnitude of the contact potential was not as accurately measured as their excellent ideas merited.

In 1905 Bjerrum[18] developed a method for correcting for liquid contact potential, which consisted in placing between the two electrode solutions a 3.5 N solution of KCl, which he called a "saturated" solution, and measuring the potential of the system, and then replacing the 3.5 N KCl solution with his so-called "half-saturated" or 1.75 N KCl solution and measuring the potential of this resulting system. He subtracted the difference between the potentials of these two systems from that of the system containing the 3.5 N solution and called the resulting extrapolated emf. practically the correct one of the system in which there is no contact potential. In certain cases he thought that the difference to be subtracted should be even larger than the value found experimentally.

---

[7] Nernst, W., The Electromotive Activity of Ions, Z. physik. Chem. vol. 4, p. 165; 1889.

[8] Planck, M., On the Potential Difference Between Two Dilute Solutions of a Binary Electrolyte, Wied. Ann., vol. 39, p. 178; vol. 40, p. 561; 1890. Ann. Physik. Chem. vol. 4, 561; 1890.

[9] Negbaur, W., Experimental Investigations on Potential Differences at the Liquid Junctions of Very Dilute Solutions, Ann. Physik. Chem., vol. 44, p. 737; 1891.

[10] Johnson, K. R., On the Nernst-Planck Theory of the Potential Difference Between Solutions, Ann. der Physik., vol. 14, p. 995; 1904.

[11] Henderson, P., On the Thermodynamics of Liquid Potentials. Z. physik. Chem., vol. 59, p. 118; 1907; vol. 63, p. 325; 1908.

[12] Cumming, A. C., The Elimination of Potential Due to Liquid Contact, Trans. Faraday Soc., vol. 2, p. 213; 1906; vol. 8, p. 86; 1912; vol. 9, p. 174; 1913.

[13] Lewis, G. N., and Sargent, L. W., Potentials Between Liquids. J. Am. Chem. Soc., vol. 31, p. 363; 1909.

[14] MacInnes, D. A., and Parker, K., Potassium Chloride Concentration Cells, J. Am. Chem. Soc., vol. 37, p. 1445; 1915. MacInnes, D. A., Liquid Junction Potentials, J. Am. Chem. Soc., vol. 37, p. 2301; 1915. MacInnes, D. A., and Yeh, Y. L., The Potentials at the Junctions of Monovalent Chloride Solutions, J. Am. Chem. Soc., vol. 43, p. 2563; 1921.

[15] Smith, E. R., Potential Differences Across the Boundaries Between Solutions of Mixed Univalent Chlorides, B. S. Jour. Research, vol. 2, p. 1137; 1929.

[16] Duschak, E., Elliott, F., and Acree, S. F., Report at St. Louis Meeting of Am. Chem. Soc.; 1920; Address Bureau of Standards; Dec. 14, 1929; Murray and Acree, B. S. Jour. Research, vol. 7, p. 713; 1931.

[17] Tower, O. F., Studies of Superoxide Electrodes, Z. physik. Chem., vol. 18, p. 17; 1895.

[18] Bjerrum, N., Elimination of Contact Potential Between Two Dilute Aqueous Solutions by Interposition of a Concentrated Solution of Potassium Chloride, Z. physik. Chem., vol. 53, p. 428; 1905; vol. 59, pp. 336, 581; 1907. Z. Elektrochem, vol. 17, pp. 58, 389; 1911.

III. ELIMINATION OF CONTACT POTENTIAL WITH SATURATED POTASSIUM CHLORIDE

With the idea of finding a single solution which is generally efficient as a contact potential eliminator, Loomis and Acree [19] tried 11 *N* ammonium nitrate, 4.12 *N* potassium chloride, 7.7 *N* potassium iodide, 5.7 *N* potassium bromide, and 4.3 *N* calcium nitrate, and showed that the 4.12 *N* or completely saturated solution of potassium chloride at 25° C. practically annuls the contact potential between 0.1 *N* KCl and various concentrations of HCl from 1 *N* down to 0.001 *N*. In other words, the contact potentials between the 4.1 *N* KCl and the more dilute solutions on either side of it must be nearly zero and nearly cancel one another, the total emf. then corresponding to the algebraic sum of the two electrode potentials within about ±1.0 mv. As we have found that the different types of liquid junctions used in routine work vary in emf. by ±1.0 mv and that another error of 1 to 2 mv is caused by hysteresis in solubilities and emf. when saturated calomel electrodes containing solid potassium or ammonium chloride are used in open air instead of in thermostats, we may safely rely upon the 4.1 *N* KCl eliminator within these emf. limits. This method has since been nearly universally adopted, especially in combination with mercury and calomel as an electrode as suggested by Michaelis and Davidoff [20] and its value has been substantiated by Harned,[21] by Fales and Vosburgh [22] in studies of the Planck formula for contact potential, and by Hitchcock,[23] although criticized by Scatchard.[24]

Other evidence showing that the Loomis-Acree method is approximately correct is found in the fact that Bjerrum, Loomis and Acree, Myers and Acree,[25] Harned, Lewis and his coworkers, and Fales and Vosburgh, cited above, have found the values 0.4273, 0.4269 and 0.4272, 0.4273, 0.4270 to 0.4274, 0.4267, 0.4272 (to 0.4257), 0.4274, and 0.4268 volts, or an average of about 0.4271 to 0.4272 volts for the potential of the system Pt-H_2-0.1 *N* HCl-0.1 *N* KCl-HgCl-Hg. The contact potential between the 0.1 *N* HCl and the 0.1 *N* KCl has been found by Bjerrum, by Myers and Acree, Murray and Acree, and by Lewis and his coworkers to average about 0.0278 volt. When this is subtracted from the 0.4271 to 0.4272 volt, it leaves 0.3993 to 0.3994 volt as the potential of this sytem with the contact potential eliminated. This value, 0.3994 volt, is very close to the values 0.3992, 0.3988, 0.3989, 0.3988, 0.3991, 0.3989, and 0.3990, or an

[19] Loomis, N. E., and Acree, S. F., A Study of the Hydrogen Electrode and of Contact Potential, Am. Chem. J., vol. 46, pp. 585, 621; 1911. Loomis, N. E., J. Phys. Chem., vol. 19, p. 660; 1915. Loomis, N. E., and Acree, S. F., J. Am. Chem. Soc., vol. 38, p. 2391; 1916. Loomis, N. E., and Meacham, M. R., J. Am. Chem. Soc., vol. 38, p. 2310; 1916. Loomis, N. E., Essex, J. L., and Meacham, M. R., J. Am. Chem. Soc., vol. 39, p. 1133; 1917.

[20] Michaelis, L., Die Wasserstoffionem-Konzentration, p. 150; 1914.

[21] Harned, H. S., The Hydrogen and Hydroxyl-Ion Activities of Solutions of Hydrochloric Acid, Sodium, and Potassium Hydroxides in the Presence of Neutral Salts, J. Am. Chem. Soc., vol. 37, p. 2460; 1915. The Hydrogen and Chlorine Activities of Solutions of Potassium Chloride in 0.1 Molal Hydrochloric Acid, J. Am. Chem. Soc., vol. 38, p. 1986; 1916.

[22] Fales, H. A., and Vosburgh, W. C., Planck's Formula for the Potential Difference Between Solutions and the Values of Certain Important Cells, J. Am. Chem. Soc., vol. 40, p. 1291; 1918.

[23] Hitchcock, D. I., The Ionization of Protein Chlorides, J. Gen. Phys., vol. 5, p. 383; 1922.

[24] Scatchard, G., Emf. Measurements with a Saturated Potassium Chloride Bridge or with Concentration Cells with a Liquid Junction, J. Am. Chem. Soc., vol. 45, p. 1716; 1923. Use of Flowing Junction to Study the Liquid Junction Potential Between Dilute Hydrochloric Acid and Saturated Potassium-Chloride Solutions, J. Am. Chem. Soc., vol. 47, p. 696; 1925.

[25] Myers, C. N., Clarke, W. F., and Acree, S. F., A study of the Hydrogen Electrode, of the Calomel Electrode, and of Contact Potential, J. Phys. Chem., vol. 20, p. 243; 1916. Myers, C. N., and Acree, S. F., J. Phys. Chem., vol. 21, p. 334; 1917.

average of 0.3990, obtained in the laboratories of Noyes,[26] Lewis, Loomis, Harned, Fales and Vosburgh, and Acree, for the system Pt-H_2-0.1 *N* HCl-HgCl-Hg. Although there is some doubt regarding minor points, such as the relation of the electrode potential to the relative solubility of calomel [27] in 0.1 *N* KCl and 0.1 *N* HCl, and the method of making sharp or mixed liquid junctions, both of which should be studied more carefully by independent experimental methods, it can at present be assumed that the emf. of the system Pt-H_2-0.1 *N* HCl-0.1 *N* KCl-HgCl-Hg with contact potential eliminated is between 0.3990 and 0.3994.

This shows that the error involved in assuming that the 4.1 *N* KCl completely eliminates the contact potential of this system is not over ±1.0 mv which is less than 4 per cent of the contact potential involved.

It thus seems that of these two methods proposed by Bjerrum and by Loomis and Acree for eliminating contact potentials by the use of potassium chloride solutions as a connecting link, the latter has the advantages of (1) simplicity and rapidity; (2) direct experimental proof that the 4.1 *N* KCl actually eliminates, within the present routine experimental errors and uncertainties of ±1 mv, the contact potential between different concentrations of HCl and KCl and other solutions containing salts; and of (3) the avoidance of any extrapolations. It should be pointed out, however, that data on which such a conclusion is based are extremely meager, and a comparison of these and other methods involving different types of junctions and solutions, especially of organic compounds, is highly desirable. This is especially the case since the 3.5 *N* potassium chloride was used by Bjerrum and others as saturated and gives emf. readings distinctly different from those obtained with the really saturated 4.1 *N* solution.

IV. COMPARISON OF THESE METHODS WITH THE SYSTEM HgCl-0.1 *N* KCl-x KCl-0.1 *N* HCl-H_2-Pt

In connection with the study of the growth of fungi on regulated culture media in 1916 we undertook a comparison of the two methods and the calculation of the contact potentials of the systems involving 0.1 *N* to 4.1 *N* and intermediate concentrations of KCl as the connecting solutions between the 0.1 *N* HCl-hydrogen electrode and the 0.1 *N* KCl-calomel electrode. Table 1 gives some of the values obtained. The general technique has been described before in papers by Loomis, Myers, Clark and Acree, Loomis and Meacham, and Loomis, Essex, and Meacham referred to above. Sharp liquid junctions were made before each emf. reading. The results show clearly (1) that the 4.1 *N* KCl solution practically completely annuls the contact potential of the system, (2) that the Bjerrum extrapolation correction is about 3 mv too large for 0.1 *N* KCl-0.1 *N* HCl, and (3) that the contact potentials of the systems containing the links 1.75 *N*, 3.5 *N*, and 4.1 *N* solutions and intermediate concentrations,

[26] Noyes, A. A., and Ellis, J. H., The Free Energy of Hydrochloric Acid in Aqueous Solution, J. Am. Chem. Soc., vol. 39, p. 2532; 1917.

[27] Calomel is more soluble in *N*/1 HCl than in *N*/1 NaCl, but it might well be that in very dilute solutions, say from *N*/10 to *N*/10,000, the same solubility and emf. will be found for equivalent concentrations of sodium, potassium, lithium, hydrogen, and other chlorides. The facts should be established experimentally first, however, instead of making the assumption found in nearly every paper published recently that the electrode potential is the same for calomel in *N*/10 HCl and *N*/10 KCl.

a, although asymtotic are nearly linear and equal to $(4.1\text{-}a)\times 2.3$ mv for 0.1 N KCl-0.1 N HCl. We have also calculated the value $(4.1\text{-}a)\times 5.6$ mv for 0.1 N KCl-N HCl from data by Fales and Vosburgh. Some data were also secured with mixtures of KCl and KNO_3 as connecting links. All of these results show that the Bjerrum extrapolation correction is over three times as large as it ought to be; and it should be stated that Professor Bjerrum himself pointed out that his method should be applied only when the extrapolation is less than 2 mv, a fact overlooked by others using it when the extrapolation is several millivolts, and the error therefore large.

TABLE 1.—*Change in emf. of the system HgCl–0.1 N KCl=x KCl–0.1 N HCl–H_2 with variation in x KCl*

Difference between potentials with 1.75 N and 4.1 N KCl	Difference between potentials with 1.75 N and 3.5 N KCl	Difference between potentials with 3.5 N and 4.1 N KCl	
		First set (old calomel electrodes)	Second set (new calomel electrodes)
Volts	*Volts*	*Volts*	*Volts*
0.00541	0.0041	0.00139	0.00123
.00546	.0042	.00126	.00120
.00582	.0045	.00122	.00120
.00538	.0041	.00132	.00121
.00561	.0043	.00129	.00135
		.00136	.00140
		.00105	
Average. .0055±2	.0042±2	.00127	.00127
Average		0.0013±1	

The results on Pt-H_2-0.1 N HCl-KCl link-0.1 N KCl-HgCl-Hg show a drop of 22.3 mv in the contact potential for the 0.1 N KCl connecting link (about 27.8 mv), down to that of 1.75 N KCl (about 5.5 mv). The difference between the contact potentials when the 1.75 N and the 3.5 N KCl solutions are used as links is then about 4.3 mv which agrees within routine experimental errors with the 3.6 mv observed by Bjerrum, 4.1 mv observed by Fales and Vosburgh, and 4.9 mv observed by Sorensen,[28] and the 4.3 mv can be considered as the average, approximate value. The difference between the contact potentials observed when the 3.5 N and 4.1 N KCl are used as links is only 1.3 mv instead of the above-named average of about 4.3 mv, the latter being the correction to be applied if the Bjerrum extrapolation method is used outside the limits set by him. In such a case it is clear that the Bjerrum extrapolation correction would be 3.3 times the true value. That this conclusion is correct is further borne out by data of Fales and Vosburgh on contact potential differences observed when different concentrations of KCl are inserted between 0.1 N KCl and 1 N HCl at 25°. Their differences in the contact potentials for the 1.75 N and 3.5 N KCl connecting solutions is 14.5−3.1 or 11.4 mv, which is 3.6 times their difference of 3.1 mv between the contact potentials for the 3.5 N and 4.1 N KCl connecting links. In this case the error in the wrong use of the Bjerrum method is about 8 mv or many times the experimental error.

[28] Sorensen, S. P. L., Enzyme Studies, Biochem. Zeit., vol. 21, p. 158; 1909.

V. ELIMINATION OF CONTACT POTENTIALS OF ORGANIC ACIDS AND ACID SALTS

Following the above measurements on the system 0.1 *N* HCl-0.1 *N* KCl, a considerable amount of work was carried on in which various buffered culture media replaced the 0.1 *N* HCl. The results clearly showed that such organic salts have very small contact potentials, less than 5 mv, toward 0.1 *N* KCl which can be estimated within ±0.5 mv by the above formula based on the Loomis-Acree method. It was, therefore, thought desirable to extend the studies to organic acids, bases, and salts of known compositions and ionic mobilities in order to secure data which will be of both (*a*) practical use in determining the hydrogen ion activities and ionization constants of sugar acids and related organic acids and bases, and also of (*b*) theoretical value in devising the best methods of forming liquid junctions and studying the underlying cause, measurement and elimination of their potentials. It was thought to be especially desirable to supplement the method used above with that of Murray and Acree [29] to see the effect of increasing concentrations of both potassium and ammonium chlorides on the asymptotic approach to the maximum elimination of the contact potentials of acid solutions having various pH values from 1 to 4. A 0.1 *N* solution of sodium acid phthalate was chosen as a reference standard. Quinhydrone was added to it and also to the other solutions whose contact potentials against the sodium acid phthalate were to be determined. The measurements were made in the open air with observations of the temperature at regular intervals and correction of all readings to 28° C. Measurements were made to learn the values of the emf., including the contact potential between *N*/10 sodium acid phthalate (pH 3.95) as a reference standard combined in pairs with 0.1 *N* HCl (pH 1.04), 0.05 *M* universal buffer solution composed of 0.05 *M* citric acid and 0.05 *M* boric acid (pH 1.95), 0.1 *M* malic acid (pH 2.16), 0.1 *M* sodium acid malate (pH 4.01) and the standard mixture of 0.1 *N* sodium acetate−0.1 *N* acetic acid (pH 4.59). Then various concentrations of ammonium chloride and potassium chloride were interposed as contact potential eliminators between the above pairs of acid solutions, and the emf. again measured. These contact potential eliminators included 0.5 *N*, 1.75 *N*, 3.5 *N*, 4.1 *N*, 5.0 *N*, and 5.66 *N* (saturated) ammonium chloride and 0.5 *N*, 1.75 *N*, 3.5 *N*, and 4.1 *N* (saturated) potassium chloride.

TABLE 2.—*Contact potentials referred to 3.5 N NH_4Cl and KCl at 28° C.*

Solution	With 0.1 *M* NaH Ph	With NH_4Cl as contact potential eliminator					
		0.5 *N*	1.75 *N*	3.5 *N*	4.1 *N*	5.0 *N*	5.66 *N*
	mv	*mv*	*mv*	*mv*	*mv*	*mv*	*mv*
N/10 HCl (pH 1.04)	−26.6	−11.6	−3.1	0	0.4	1.0	2.6
M/20 universal buffer (pH 1.95)	−17.7	----------	−.6	0	1.2	.7	1.6
M/10 malic acid (pH 2.16)	−7.9	−4.1	.6	0	.2	.6	1.2
M/10 NaH malate (pH 4.01)	−1.6	----------	−.1	0	−1.1	−.2	−.4
N/10 NaAc.HAc (pH 4.59)	−1.1	----------	1.0	0	0	−.4	−.5
		With KCl as contact potential eliminator					
N/10 HCl	−26.6	−13.1	6.0	0	−0.3	----------	----------
M/10 malic acid	−7.9	−1.7	−.5	0	+.2	----------	----------
N/10 NaAc.HAc	−1.1	−1.3	−.1	0	−.2	----------	----------

[29] Murray, C. N., and Acree, S. F., Elimination of Contact Potential by Means of Saturated Ammonium Chloride and Potassium Chloride. B. S. Jour. Research, vol. 7, p. 713; 1931.

Table 2 shows the magnitude of the changes in emf. produced by the insertion of each contact potential eliminator between the pairs of acids, all of the reductions of emf. being referred to that of the 3.5 *N* solution as a base line. The 4.1 *N* solution could also be used for reference. The difference between the residual contact potentials for 1.75 *N* and 3.5 *N* contact potential eliminators is not very large but can not be neglected for the very acid solutions. But eliminators varying from 3.5 *N* to 5.66 *N* produce nearly the same contact potential within the usual experimental error of about ±1 mv in these routine methods. The more acid solutions seem to show a slight increase in contact potential with increase in concentration of the eliminator and this is being measured more accurately by precision work under way in a constant temperature bath under better-controlled conditions.

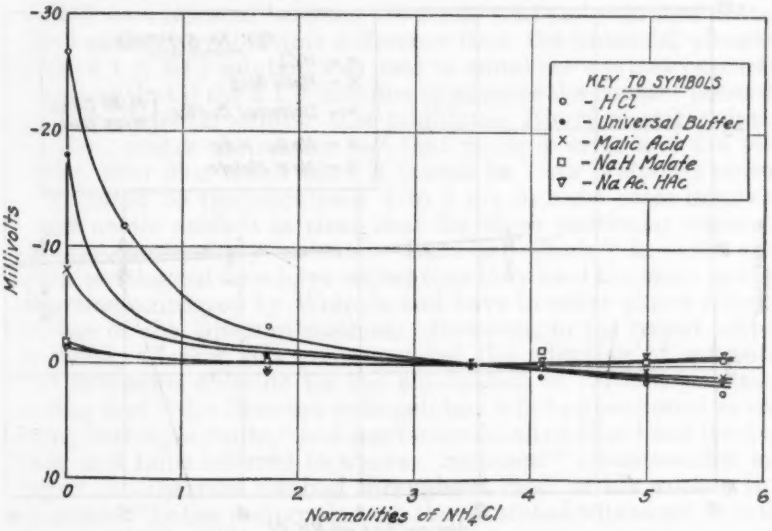

FIGURE 1.—*Relation between concentration of contact potential eliminator and change in the contact potentials of M/10 sodium acid phthalate and several buffers with different pH values*

Figure 1 gives some smooth curves for the above-named five acid solutions which show the wide divergence of the contact potentials with no eliminators and a gradual asymptotic approach or merging of all curves as the eliminator is increased in concentration. The 3.5 *N* concentration was chosen as a base line because of its historical significance and its position near the beginning of the series of concentrated eliminators which nearly annul the contact potentials. Figure 2 gives a composite graph which represents the best smooth curve for all the data on the assumption that it should be asymptotic and can represent a uniform effect of the contact potential eliminator on all solutions. Probably neither of these assumptions, especially the second one, is exactly true, but such a curve gives at least a first approximation, pending precision work, which shows that 4.1 *N* and higher concentrations of ammonium or potassium chloride certainly annul the contact potentials of all usual buffers, culture media, etc.,

to within about ±0.5 to 1 mv. If the most concentrated eliminators under annul or even over annul the contact potential by a nearly fixed amount in certain cases, or asymptotically approach any such state, this excess emf. when known can be included as a part of the emf. of the standard electrode.

If sufficient acid or alkali or a buffer is added to the eliminator to make its pH close to that of the solution studied, or if sufficient ammonium or potassium nitrate or sodium chloride is added to the eliminator to offset the effect of the difference in the mobilities of the ions of the eliminator and of the other solutions, a more nearly perfect elimination of contact potential will be effected. The compositions of ammonium chloride-ammonium nitrate mixtures necessary to annul the contact potentials of various concentrations of sodium acetate-acetic acid solutions have been calculated by use of the Hen-

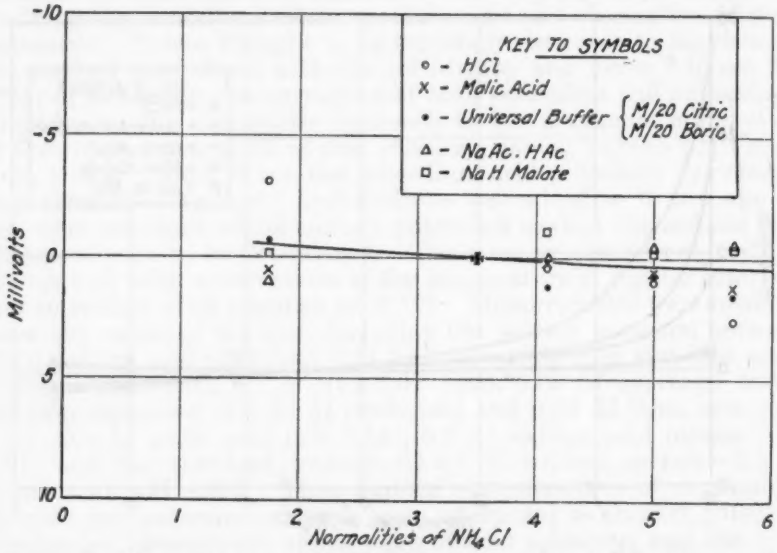

FIGURE 2.—*Composite curve for the relation between the concentration of the contact potential eliminator and the deviation of the contact potentials from those found with 3.5 N NH_4Cl*

derson equation. As the concentration of the sodium acetate-acetic acid solutions becomes less, the calculated ammonium chloride-ammonium nitrate ratios approach an isoelectric mixture; that is, one in which the mobility of the ammonium ions is exactly balanced by the joint effect of the mobilities of chloride and nitrate ions. Such isoelectric mixtures calculated from the transference numbers accepted for dilute solutions with various normalities of ammonium ion contain approximately 76.2 *M* per cent ammonium chloride and 23.8 *M* per cent ammonium nitrate. The use of these isoelectric mixtures for various normalities of eliminator from 0.1 to 0.001 *N* gives calculated contact potentials which are less than when ammonium chloride only is used and which approach zero as the concentration of the isoelectric mixture increases. Similar calculations have been made for hydrochloric acid solutions. These calculations and experimental studies based upon them will be reported in another article

of this series. We suggest the use of transference numbers measured at the respective higher concentrations instead of the corresponding ionic mobilities in the derivation and use of formulas similar to that of Henderson.

VI. DISCUSSION OF STANDARDIZATION ON ONE METHOD OF ELIMINATING CONTACT POTENTIAL

For the purposes of uniformity of published data one method should be adopted for the elimination of contact potential. The saturated (4.1 *N*) potassium chloride solution has been widely recommended and employed. In some instances, however, the extrapolation method is still used. In an excellent article Walpole [30] used the 4.1 *N* KCl solution in the measurement of the ionization of acetic acid,[31] but he also measured the contact potential differences when the 1.75 *N* and 3.5 *N* KCl were inserted between the acetic acid and standard acetate solutions and subtracted this difference from the potential observed when the 4.1 *N* KCl solution was used to annul the contact potential. It is obvious that if the 4.1 *N* solution eliminates the contact potential within experimental errors, this additional Bjerrum extrapolation (correction) makes the results just that much in error and the total correction over four times what it should be. As Walpole's correction amounted to the calculated 3 to 5 mv in some cases involving HCl and acetic acid, it is clear that for these particular cases the results are considerably in error. Lubs and Clark [32] in their work along bacteriological lines have stated that they used the same method of correction employed by Walpole and have in other places referred to the use of the Bjerrum method. However, in the recent edition of his book, Clark [33] has recommended the adoption of saturated (4.1 *N*) potassium chloride for the elimination of contact potential, predicting that "the Bjerrum extrapolation will be abandoned as contributing nothing definite," and has recalculated on that basis the data of Clark and Lubs referred to above. Sörensen [34] recommended and employed the Bjerrum method throughout most of his work. In a recent article [35] he has preferred to use the saturated potassium chloride solution method. Büilmann [36] in his well-known researches on the quinhydrone electrode has used the Bjerrum extrapolation method to eliminate liquid junction potentials. Schmidt and Hoagland [37] state that "for very accurate work the extrapolation method of Bjerrum gives the closest approximation." Prideaux [38] in his book on indicators refers repeatedly to the use of the Bjerrum method as being the correct one. Michaelis [39] recommends the Bjerrum method in his latest book on hydrogen-ion measurements. There are numerous

[30] Walpole, G. S., Hydrogen Potentials of Mixtures of Acetic Acid and Sodium Acetate, J. Chem. Soc., vol. 105, pp. 2501, 2521; 1914.
[31] Preliminary Measurements on Acetic Acid and Aniline had been reported by Loomis and Acree, Am. Chem. J., vol. 46, p. 621; 1911, and Loomis, N. E., J. Phys. Chem., vol. 19, p. 660; 1915.
[32] Clark, W. M., and Lubs, H. A., Hydrogen Electrode Potentials of Phthalate, Phosphate, and Borate Buffer Mixtures, J. Biol. Chem., vol. 25, p. 479; 1916.
[33] Clark, W. M., The Determination of Hydrogen Ions, p. 461; 1928.
[34] Sörensen, S. P. L., and Linderstrom-Lang, K., The Determination and Value of p_H in Electrometric Measurements of Hydrogen-Ion Concentrations, Compt. rend. trav. lab. Carlsberg, vol 15, p. 40; 1924.
[35] Sörensen, S. P. L., Linderstrom-Lang, K., and Lund, E., The Influence of Salts upon the Ionization of Egg Albumin, J. Gen. Physiol., vol. 8, p. 543; 1927.
[36] Büilmann, E., The Quinhydrone Electrode and its Applications, Bull. Soc. Chim. (4), vol. 41, p. 224; 1927.
[37] Schmidt, C. L. A., and Hoagland, D. R., University of California Publications in Physiology, vol. 5, p. 29.
[38] Prideaux, E. B. R., Theory and Use of Indicators, p. 46; 1917.
[39] Michaelis, L., and Perlzweig, W. A., Hydrogen Ion Concentration, pp. 174-182; 1926.

other instances in the literature where the authors state that they have employed the Bjerrum extrapolation to annul the contact potential. Even though in most work with buffered media the error is small, the use of a wrong principle will make the errors large in other cases. In the future there should be no doubt in the minds of workers in these fields that the use of the 4.1 *N* (saturated) potassium chloride solution or especially of (3 *N* KCl+*N* KNO_3) is both more reliable and much more convenient.

VII. SUMMARY

The Bjerrum method of correcting for contact potential by the use of an extrapolated value and the Loomis-Acree method of eliminating contact potential by the use of 4.1 *N* (saturated) potassium chloride solution are compared for the system HgCl-0.1 *N* KCl-x KCl-0.1 *N* HCl-H_2-Pt, and for systems in which organic acids and acid salts replace the highly ionized hydrochloric acid. In view of the greater accuracy, simplicity, and rapidity of the Loomis-Acree method and its avoidance of uncertain extrapolations, its adoption for general use is recommended in order to insure uniformity of published data. An approximately isoelectric eliminator, such as 3 *N* KCl+*N* KNO_3, should be used between solutions with pH values between 3 and 10,

WASHINGTON, November 7, 1931.

RP404

AN ELECTROSTATIC VOLTMETER

By Warren W. Nicholas

ABSTRACT

An electrostatic voltmeter possessing several unique features is described. The size is a minimum for such instruments, since the potential difference is applied to two electrodes, the geometrical arrangement of which is analogous to concentric spheres. The inner electrode is supported on the end of an insulating bushing introduced through the outer electrode, which is a metal can. The inner electrode contains a suspended dumb-bell rotated by electrostatic repulsion, as in the Coulomb torsion balance. The deflection is read by means of a mirror, which, for convenience in mounting the instrument at a safe height, may be placed at the lower end of the insulating bushing. For purposes of automatic control, the dumb-bell may be connected mechanically with an apparatus at ground potential. The design may be adapted to the use of high gas pressures, desirable in the measurement of very high voltages. The sensitivity of the instrument is discussed and calibration curves given for various suspensions.

So many and such varied types of electrostatic voltmeters are described in the literature that the value of publishing a new design may well be questioned. However, it is a matter of common observation that the design for a simpler, less expensive, or more easily constructed instrument is always of considerable interest to investigators; this is probably chiefly due to the fact that the average worker spends a considerable share of his time and energy trying to improve the design of his apparatus. Accordingly, an electrostatic voltmeter is here described which seems to possess several points of unique interest. The writer has used instruments of this design for several years with entire satisfaction. Many of the details are not original, the ideas being accumulated in the X-ray laboratories at Stanford, Cornell, and Columbia.

In Figure 1 is shown a vertical section through the instrument. A circular metal base B is supported on three insulators A by means of leveling screws. Resting on B and inclosing the system C is an inverted metal can H which protects C from dust and air currents and fixes the electrical characteristics of the inside of the instrument (that is, if the can were omitted, the electrical fields near C would depend to some extent on the distribution of charge over the walls of the room and the furniture, and this distribution would be expected to vary with weather conditions and arrangement of furniture). Through the center of B passes an insulating bushing I which supports the moving system. This latter is hung from the suspension S, and consists of a dumb-bell K, a stiff wire W passing down through the center of the insulating bushing, a disk V immersed in a light oil for damping, and a mirror M, by means of which the displacement of the moving system may be read optically. The moving system should be of reasonably light weight and small moment of inertia in order to reduce strains on the suspension, and to minimize the period of oscillation.

In Figure 2 are shown a vertical section (above) and a horizontal section (below) through C. To the base F are fastened the cylinders L; the deflection of the moving system is due to the electrostatic repulsion between L and K. The mechanism at D provides a means for adjusting the angle θ_0 at which the dumb-bell is permanently set (position for zero applied voltage). The various parts of C are designed so as to eliminate all sharp corners and edges from which brush discharge might take place; to this end both the suspension S and the part of the wire W which projects above F are inclosed in

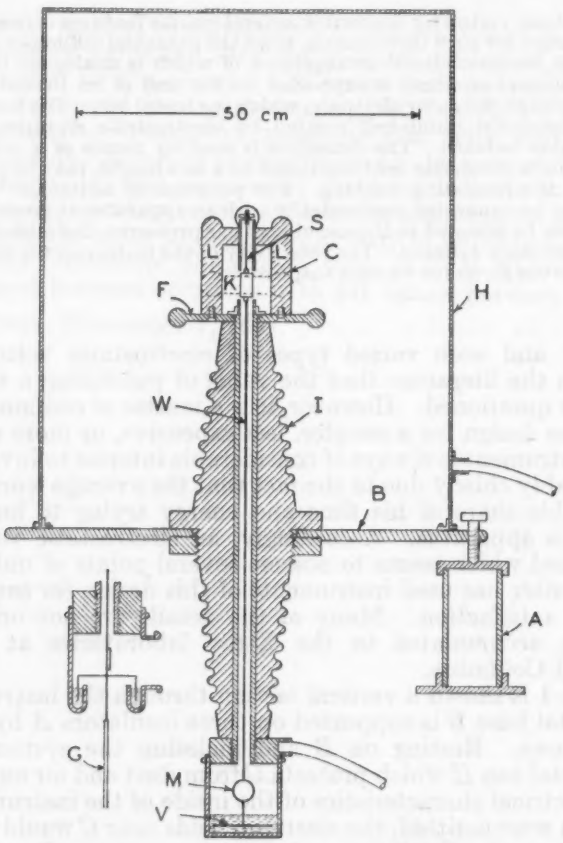

FIGURE 1.—*Vertical section through voltmeter*

tubes T and U, and D is covered with a rounded cap. So far as possible all insulating materials inside the can H must be electrically shielded from the repulsion system K and L, for the variation of the potential of a surface not thus shielded would vary the electrical fields near K and L, and consequently the deflection. A slight amount of brush discharge (or perhaps even the residual ionization) might conceivably cause such variations of potential on a surface of excellent insulating properties, but probably the most noticeable effect would be found when the voltage on the instrument was changed. Such a change requires a readjustment of surface charges throughout

the instrument, and this readjustment would require a period of time in the case of an insulating surface.[1]

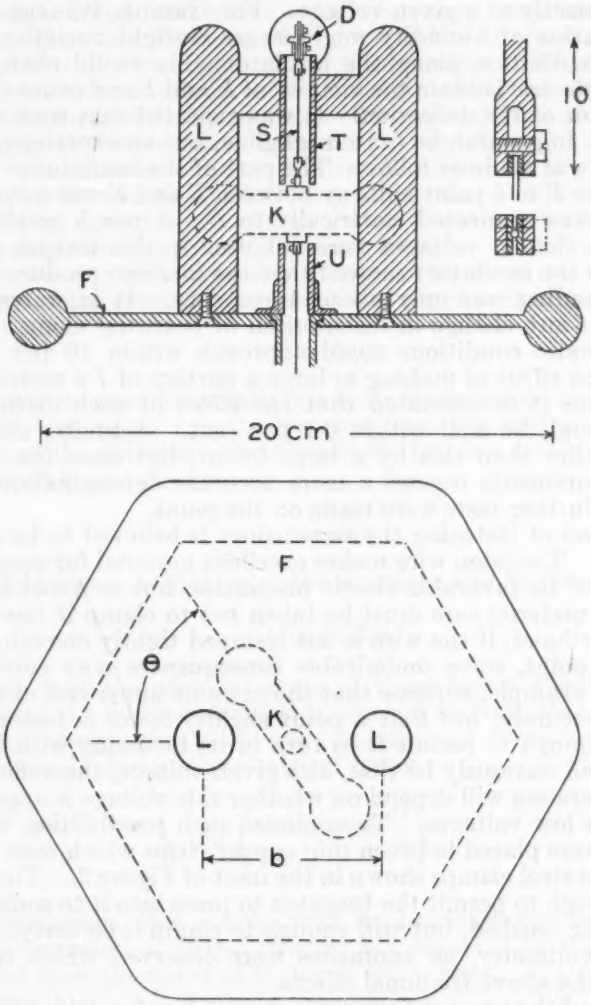

FIGURE 2.—*Upper figure, vertical section. Lower figure, horizontal section*

The presence of part of the insulating bushing *I* inside of *H* can not be avoided, of course; in order to shield *K* and *L* from the electric

[1] The writer has experienced analogous difficulties in connection with the use of a galvanometer in the high tension circuit (usually at the cathode potential) for the purpose of measuring the cathode ray current in X-ray tubes. The galvanometer was of the wall type, having a wooden back and a large glass front both very close to the moving coil. Whenever the cathode potential was varied the deflection would be markedly disturbed, but would drift slowly back to the correct value. The disturbances were prevented by electrical shielding of the moving system from insulated surfaces. Galvanometers similar to Leeds & Northrup type R have not been shown to be appreciably subject to such disturbances, but nevertheless even when instruments of this design are used by the writer in a high-voltage system, the glass front is shielded from the moving coil (except for a small hole in front of the mirror) and also a bent strip of sheet metal is slipped down into the hole containing the lower suspension and connected electrically to the magnets or case. In some galvonometers the case itself is found to be insulated from the electrical circuit; this condition should be remedied.

fields due to the distribution of potential along the surface of I, the base F is extended well beyond the cylinders L. The question may well be raised whether the distribution of potential along I always duplicates exactly at a given voltage. For example, it is conceivable that a variation of humidity might cause a slight variation of the potential distribution along the insulator; this would change very slightly the electric fields in the vicinity of K and L and cause a change in the amount of the deflection. It was expected that such disturbances would, in general, be quite negligible, but an experimental test of the point was made as follows: The part of the insulator extending from the base B to a point halfway between B and F was wound with wire which was connected electrically to B. A rough recalibration up to 25 kv. (higher voltages were not used in this test on account of danger to the insulator) showed that the increase produced in the voltmeter reading was only about 1 per cent. It is scarcely conceivable that any change in distribution of potential along I due to varying climatic conditions could approach within 10 per cent of producing the effect of making so large a portion of I a metallic conductor. Thus it is estimated that the effect of such disturbances will, in general, be well within 0.1 per cent. Actually, the errors may be smaller than this by a large factor, but since few, if any, X-ray measurements require a more accurate determination of the voltage, no further tests were made on the point.

The method of fastening the suspensions is believed to be of some importance. Tungsten wire makes excellent material for suspensions on account of its favorable elastic properties, but to avoid crushing such brittle material care must be taken not to clamp it too tightly. On the other hand, if the wire is not clamped tightly enough, and at the correct point, some undesirable consequences may conceivably occur. For example, suppose that the extreme upper end of the wire is clamped securely, but that a point slightly lower is fastened just insecurely enough to permit it to turn in its fastening with friction. The effect will obviously be that, at a given voltage, the deflection of the moving system will depend on whether this voltage is approached from high or low voltages. To minimize such possibilities, the ends of the wire were placed between thin copper strips which were pressed tightly in the steel clamps shown in the inset of Figure 2. The copper was soft enough to permit the tungsten to press into it to some extent without being crushed, but stiff enough to clamp it securely. In the use of the voltmeter, no anomalies were observed which could be ascribed to the above frictional effects.

A feature of the present design which may be of considerable value for some purposes is that the deflection of the moving system may be readily transmitted mechanically to an apparatus electrically grounded. In the inset of Figure 1 is indicated a means for doing this. By a slight modification of the construction of the damping disk and oil cup, the lower end of the moving system may be attached to a light glass rod G, the lower end of which may be at low voltage. By this means, for example, a sensitive relay system could be operated so as to provide a rough control of the voltage. Or a device could be readily constructed by means of which the power would be cut off if the voltage exceeded or decreased below certain limits; this would be useful in cases where an apparatus is run without constant attention.

It is of no value to attempt to determine theoretically the constants of the present voltmeter for purposes of calibration, for the sensitivity is obviously not readily calculated with any considerable accuracy. However, a rough and naive calculation may facilitate the understanding of certain details of the action of the instrument, and guide the selection of dimensions in modified designs. When a potential difference V is maintained between the system C and the can H each ball on the dumb-bell K acquires a charge q and each of the cylinders L is charged; the electrical fields near K and L may be regarded as chiefly due to these charges. Let us consider the repulsion of the charge q in the electric field of the cylinders L. It is well known that the force on a very small charge q at a distance a from a long thin wire having a charge ρ per unit length is $2\rho q/a$. For a rough approximation, we may identify these charges with those on the balls and cylinders of the present instrument and suppose that

$$F = 2\rho q/a$$

is the force on one of the balls due to its electrical repulsion by one of the cylinders, where a is the distance from the center of the ball to the axis of the cylinder. Now when the ball is a distance a from one cylinder, it is at a distance

$$\frac{a}{\tan \Theta/2}$$

from the other. Accordingly, the repulsion due to this second cylinder is

$$F \tan \Theta/2$$

Noticing that the moment arms of these forces about the axis of rotation of the dumb-bell are $(b/2)\cos\Theta/2$ and $a/2$, that $a = b \sin \Theta/2$, and remembering that there are two balls and two cylinders, we find for the couple due to the electrical forces

$$Fa\left(\frac{1}{\tan\frac{\Theta}{2}} - \tan\frac{\Theta}{2}\right)$$

For equilibrium, this couple must be balanced against the torsion of the suspension, $k\ (\Theta - \Theta_0)$, where k is a constant for a given suspension and Θ_0 is the value of Θ for $V = 0$. Thus,

$$\Theta - \Theta_0 = \frac{Fa}{k}\left(\frac{1}{\tan\frac{\Theta}{2}} - \tan\frac{\Theta}{2}\right)$$

Now, in substituting for F in terms of ρ and q, it is obvious that all charges on the system C will be proportional to V if the dumb-bell

is kept at any constant deflection. Accordingly, we may write

$$\rho q = gV^2\psi(\Theta)$$

where g is a constant.[2]

The factor $\psi(\Theta)$ is introduced to allow for the approximations made in assuming infinitely long cylinders, neglecting induction and screening effects, etc. One obvious cause for the variation of ψ with Θ is that as the balls approach the cylinders the charges q and ρ will decrease due to electrostatic induction. Over the range of deflections ordinarily used, however, ψ would not be expected to vary by a large factor. (Compare fig. 3.) Thus we have finally

$$\Theta - \Theta_0 = \psi(\Theta)\cdot\frac{2g}{k}\left(\frac{1}{\tan\frac{\Theta}{2}} - \tan\frac{\Theta}{2}\right)\cdot V^2 \qquad (1)$$

For small deflections, the variation in the multiplier of V^2 is negligible, so that the deflection, $\Theta-\Theta_0$, is closely proportional to the square of the voltage. For very high voltages, the dumb-bell can never be deflected beyond $\Theta=\frac{\pi}{2}$. The maximum possible deflection, $\frac{\pi}{2}-\Theta_0$, is approached asymtotically as V approaches infinity, and at the same time the sensitivity approaches zero.

The dimensions of the completed instrument were as follows: $R=29$ cm; $r=1.5$ cm; $s=1.6$ cm; $b=9.0$ cm. For purposes of test, three different suspensions of tungsten wire were used with diameters and lengths as follows: 0.25 mm, 27 mm, 0.12 mm, 32 mm, 0.05 mm, 32 mm. The values of the torsion constants (k) expressed in dyne cm degree^{-1} were, respectively, 280, 23, and 0.52. These figures, together with the calibration curves of Figure 3 provide all the data necessary for a determination of ψ and its variation with Θ; this function ψ (Θ) is shown in the inset of Figure 3. It is to be remembered, of course, that V is expressed in electrostatic units in the formulas. At the higher voltages, an audible brush discharge began. The voltage at which this occurred depended on Θ; thus with the various suspensions, 0.25 mm, 0.12 mm, 0.05 mm, it began at about 95, 80, and 60 kv, respectively. This variation is of course connected with the variation with Θ of the electric fields near the balls and cylinders, as indicated by the function ψ (Θ).

---

[2] The order of magnitude of g may be estimated as follows: Imagine the entire system C replaced by a metal sphere of radius P. The charge σ per unit area on this sphere would be, with fair approximation, since there would be no other charged bodies inside H,

$$\frac{VR}{4\pi P(R-P)}$$

where R is the radius of the can H and V is the difference of potential between H and C. Now the system of conductors actually composing C may be thought to approximate, electrically, a spherical network of radius P equal to about 10 cm in the present construction. Thus the surface charge densities on the outward-facing portions of the cylinders and balls will be roughtly equal to σ, or allowing for the electrical shielding of inward-facing surfaces, we may suppose the effective charge over the surfaces of balls and cylinders to be of the order of $\sigma/2$. Accordingly, taking surface areas into account, $q=4\pi s^2\cdot(\sigma/2)$ and $\rho=2\pi r\cdot(\sigma/2)$, where s and r are the radii of balls and cylinders, respectively. We thus find the order of magnitude of g to be

$$\frac{rs^2R^2}{8P^2(R-P)^2}$$

It is of interest to note that formula (1) is of the form

$$\frac{V}{\sqrt{k}} = f(\Theta, \Theta_0, R, P, s, r)$$

This shows that, for a given instrument, and for a given zero setting, θ_0, the characteristics are completely described by a function of $V/\sqrt{k}$. Thus only one of the three calibration curves of Figure 3 is required (provided it extends to a sufficient range of angles); all other curves, for various suspensions can immediately be obtained from the one, by multiplying the scale of abscissas by a factor equal to the ratio of the square roots of the torsion constants. This relation may be of value in selecting a suitable suspension; the adjustment of Θ_0 is not ordinarily of sufficient precision to make the relation of much value in the final calibration.

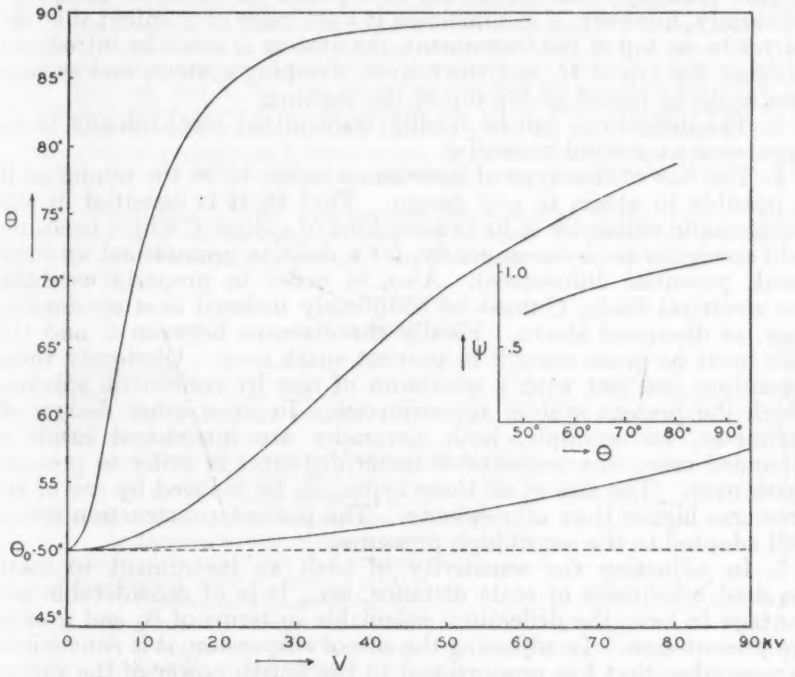

FIGURE 3.—*Calibration curves for various suspensions.*

The calibration of the present instrument was carried out by means of the high resistance described by Taylor.[3] If an especially accurate calibration is required, or if the calibration is made by a method less accurate than that used here, the data may be smoothed by any of several methods. One of these methods is to carry out the calibration in 1 kv steps and take first and second differences between the successive values of the deflection. Irregularities will usually appear in the second differences; these irregularities can be made to disappear by a slight adjustment of the data. Another method is to

[3] L. S. Taylor, B. S. Jour. Research, vol. 5 (RP217), p. 609; 1930.

approximate the data with some readily calculable function; if the approximation is close enough over a moderate range of voltage, a plot of the differences between observed and calculated values will reveal irregularities. These irregularities can then be smoothed out by graphical methods.

In conclusion, some of the advantages of the present instrument are:

1. Only one insulating bushing is required in the construction.

2. The location of the mirror and damping system in the lower end of the instrument is convenient in several ways: It permits the mounting of the voltmeter at a considerable height, which is desirable for safety and for conservation of floor space. Also the mirror and oil are in a location convenient for adjustment without removing H (the viscosity of the oil should be adjusted for optimum damping). Obviously, however, if in some case it were more convenient that the mirror be on top of the instrument, the system C could be introduced through the top of H, and the mirror, damping system, and suspension could be placed at the top of the bushing.

3. The deflections can be readily transmitted mechanically to an apparatus at ground potential.

4. The size of this type of instrument seems to be the minimum it is possible to attain in any design. That is, it is essential in any electrostatic voltmeter to have some kind of system C which measures field strengths (and consequently, for a definite geometrical arrangement, potential differences). Also, in order to properly establish the electrical fields, C must be completely inclosed in a conducting case, as discussed above. Finally the distance between C and the case must be great enough to prevent spark over. Obviously these conditions are met with a minimum of size by concentric spheres, which the present system approximates. In some other designs of voltmeter, for example, both electrodes are introduced inside a grounded case; this necessitates larger distances in order to prevent spark over. The size of all these types can be reduced by use of air pressures higher than atmospheric. The present construction seems well adapted to the use of high pressures.

5. In adjusting the sensitivity of such an instrument to meet required conditions of scale distance, etc., it is of considerable advantage to have the deflections calculable in terms of Θ_0 and k as is the present case. In adjusting the size of suspension, it is convenient to remember that k is proportional to the fourth power of the radius of the wire used as suspension, and to the inverse square of the period of oscillation of a given suspended system.

WASHINGTON, October 15, 1931.

THE HEATS OF COMBUSTION OF METHYL AND ETHYL ALCOHOLS

By Frederick D. Rossini

Abstract

The heats of combustion of gaseous methyl and ethyl alcohols, at saturation pressure, from their mixture with air, under a constant total pressure of 1 atmosphere, were found to be 763.68 ± 0.20 for methyl alcohol at 25° C. and $1,407.50 \pm 0.40$ for ethyl alcohol at 32.50° C., in international kilojoules per mole. By combining with these data the heats of vaporization recently determined by Fiock, Ginnings, and Holton and correcting the data for ethyl alcohol to 25° C., the heats of combustion of the alcohols in the liquid state are computed to be 726.25 ± 0.20 for methyl alcohol and $1,366.31 \pm 0.40$ for ethyl alcohol, at 25° C. and a constant pressure of 1 atmosphere, in international kilojoules per mole. With the factor 1.0004/4.185 these values become, respectively, 173.61 ± 0.05 and 326.61 ± 0.10 kg-cal$_{15}$ per mole.

It was found that a rapid and accurate determination of the ratio of carbon to hydrogen in a volatile organic liquid can be made by saturating a stream of inert gas with the vapor of the liquid and then passing the mixture through hot copper oxide.

CONTENTS

		Page
I.	Introduction	119
II.	Method	120
III.	Units, factors, atomic weights, etc	120
IV.	Chemical procedure	121
	1. Purification and analysis of the alcohols	121
	(a) Methyl alcohol	121
	(b) Ethyl alcohol	122
	2. Purity of the combustion reaction	123
	3. Determination of the amount of reaction	124
V.	Calorimetric apparatus and procedure	124
VI.	Calorimetric data on methyl alcohol	127
	1. Correction experiments	127
	2. Electrical energy experiments	127
	3. Combustion experiments	127
	4. Results of the present work	129
	5. Data of previous investigators	130
VII.	Calorimetric data on ethyl alcohol	132
	1. Correction experiments	132
	2. Electrical energy experiments	132
	3. Combustion experiments	134
	4. Results of the present work	134
	5. Data of previous investigators	135
VIII.	Conclusion	138
IX.	Acknowledgments	138
X.	Bibliography	138

I. INTRODUCTION

With the development of the third law of thermodynamics, by means of which values of the entropy of pure substances can be calculated from data on their heat capacities down to low tem-

peratures,[1] it has become possible to compute the free energy of formation of many organic compounds. For such a calculation there are required values for $\Delta S°_T$, the entropy of formation, and $\Delta H°_T$, the heat of formation of the compound. The former is obtained from values of $S°_T$, the entropy, at $T°$K, of the compound and of the elements from which it is formed; and the latter is computed from the heat of combustion of the compound (and the heats of formation of water and carbon dioxide) at $T°$K.

Because the heat of formation of an organic compound is usually only a small fraction of its heat of combustion, it is necessary that the heat of combustion be known with considerable accuracy in order that the uncertainty in the value of the heat of formation shall not contribute an error to the calculated free energy greater than that contributed by the uncertainty in the entropy values.

The present work is an effort to establish with the necessary accuracy the heats of combustion of methyl and ethyl alcohols, because the existing data are markedly discordant. In the case of methyl alcohol, the high and low values reported by competent investigators differ by some 1½ per cent.[2] A similar spread of the data exists in the case of ethyl alcohol, where the results of the latest two investigations differ by one-half per cent.[3]

II. METHOD

In the present investigation, alcohol vapor was burned at constant pressure in a reaction vessel in the calorimeter. The selection of gaseous rather than liquid alcohol for combustion was made because an accurate apparatus for the combustion of gases was already assembled (2),[4] and because the heats of vaporization of methyl and ethyl alcohols were being determined in another division of this bureau (3). The alcohol was carried as a vapor into the reaction vessel in the calorimeter by a stream of purified air. There the combustible mixture, ignited by means of a spark, burned quietly in a flame at the burner tip. Most of the water formed was condensed to liquid in the reaction vessel, while all of the carbon dioxide and some water vapor were carried out of the calorimeter by the excess gas.

The thermal effect produced in the calorimeter system by the heat liberated in the combustion was duplicated with electrical energy under identical calorimetric conditions.

III. UNITS, FACTORS, ATOMIC WEIGHTS, ETC.

The fundamental unit of energy employed in the present work, and the factors used to convert this unit into other commonly used units of energy, are given in previous papers (2).

The atomic weights of carbon, hydrogen, and oxygen are taken as 12.000, 1.0078, and 16.0000, respectively (4). One mole of CO_2 (44.000 g) is taken as equivalent to 1 mole of CH_3OH, or to one-half mole of C_2H_5OH.

---

[1] For qualifications and restrictions upon the application of the third law of thermodynamics in computing entropy values, see (1).

[2] These data are discussed at length on p. 129.

[3] These data are discussed in detail on p. 134.

[4] The figures in parentheses here and throughout the text relate to the reference numbers in the bibliography given at the end of this paper.

The heat capacities of methyl alcohol vapor at 25° C. and of ethyl alcohol vapor at 32.5° C. are taken as 47 and 68 joules per mole per degree, respectively.[5]

The heat capacities of liquid methyl and ethyl alcohols, and their heats of vaporization, are taken from the data of Fiock, Ginnings, and Holton (3).

All other auxiliary data are the same as previously used by the present author (2).

IV. CHEMICAL PROCEDURE

1. PURIFICATION AND ANALYSIS OF THE ALCOHOLS

(a) METHYL ALCOHOL

The methyl alcohol used in the present investigation was prepared from a sample of the best synthetic material available, by distillation in a 30-plate bubbling-cap still (6). Only the middle portion of the distillate was used. As reported in another investigation on the thermal properties of this methyl alcohol (3), the purified sample had a density ($d_4^{20}=0.79133$) practically identical with the "best" value ($d_4^{20}=0.79134$) given in the International Critical Tables (7).

Because of the variable amounts of methyl alcohol vapor (1 to 2 mg) which came through unburned during the sparking period, it was not possible to make an accurate determination of the ratio of carbon to hydrogen in the methyl alcohol by combustion in the calorimetric reaction vessel.[6] Accordingly, a series of combustion analyses to determine the ratio of carbon to hydrogen in this methyl alcohol was made by passing the alcohol vapor, carried by a stream of helium gas, through copper oxide at 600° to 700° C., and absorbing the water and carbon dioxide formed in "dehydrite" ($Mg(ClO_4)_2 \cdot 3H_2O$) and "ascarite" (a sodium hydroxide-asbestos mixture), respectively.

The complete train for these experiments consisted of the following: (*a*) A cylinder of helium gas; (*b*) a preheating furnace containing copper oxide at 700° to 800° C.; (*c*) an absorbing tube containing "ascarite"; (*d*) a tube containing "dehydrite"; (*e*) a tube containing phosphorus pentoxide; (*f*) a vessel for saturating the helium gas with methyl alcohol vapor (this saturator was arranged with a by-pass to permit flow of the helium gas without carrying any alcohol); (*g*) a quartz tube, 30 inches long, filled with copper oxide kept at 600° to 700° C.; (*h*) a condensing chamber for collecting, temporarily, the water which condensed to liquid during the combustion period;[7] (*i*) a U tube containing "dehydrite" and phosphorus pentoxide; (*j*) a second U tube containing "ascarite" and phosphorus pentoxide; and (*k*) a guard tube containing, in order, phosphorus pentoxide, "dehydrite," and "ascarite."

In carrying out an analysis with this apparatus the entire system was first flushed out and filled with helium; the weighed U-tube absorbers, filled with helium, were put in place, and a blank determination was made with helium flowing through the train. In the combustion period the helium was passed through at such a rate that 1 g of methyl alcohol was carried into the reaction region in about 30

[5] Extrapolated from the data given in (5).
[6] The details of such analyses are given in the following part of this section, under ethyl alcohol.
[7] The combustion was carried on at such a rate that the amount of water formed was greatly in excess of that which was necessary to saturate the stream of gas at room temperature.

minutes. When a sufficient amount of alcohol had been burned, as determined by inspection of the amount of carbon dioxide absorbed in the "ascarite," the helium was by-passed around the liquid methyl alcohol, and the flow of helium was continued until all of the water had been transferred from the condensing chamber to the first U tube, which contained "dehydrite." The method of weighing the absorbing tubes and correcting the observed increases in weight to vacuum in order to obtain the true masses of water and of carbon dioxide has already been described (2). Tests showed the absence of carbon monoxide in the products of combustion.[8] The amounts of carbon dioxide collected in the six experiments varied from 0.5 to 3.5 g.

TABLE 1.—*Ratio of carbon to hydrogen in the methyl alcohol*

Experiment	Mass of H_2O	Mass of CO_2	$\frac{2 \text{ (moles } CO_2)}{\text{(moles } H_2O)}$	Deviation from mean
	g	g		
1	2.13165	2.60363	1.00021	0.00027
2	1.24489	1.51875	.99904	−.00090
3	1.76721	2.15803	.99999	.00005
4	2.37995	2.90600	.99989	−.00005
5	2.83170	3.46040	1.00070	.00074
6	.43463	.53065	.99980	−.00014
Mean [1]			.99994	±.00036

[1] Omitting the results of experiments 2 and 5 gives 0.99997±0.00013.

The results of these analyses, given in Table 1, show that the ratio of carbon to hydrogen in this sample of methyl alcohol was that required by the formula CH_3OH, within the limits of precision of the determination (±0.03 per cent).

(b) ETHYL ALOCHOL

The purification of the ethyl alcohol has already been described (3). The sample used in the present investigation was from the middle portion of the distillate from the 30-plate column. From a measurement of the density of this sample ($d_4^{20}=0.78946$) and the data given by Osborne, McKelvey, and Bearce (8) for the densities of pure ethyl alcohol and mixtures of it with water, Fiock, Ginnings, and Holton (3) computed the amount of water in the alcohol to be 0.038 per cent by weight.

In order to check this value, the data from the combustion experiments in the calorimetric reaction vessel were used to compute the ratio of carbon to hydrogen in this sample of ethyl alcohol. Because, under the conditions of the experiments, ethyl alcohol ignited more quickly than did methyl alcohol, the amounts of ethyl alcohol which came through unburned during the sparking period were small (about 0.6 mg) and practically constant. In this connection experiments were made which showed that no alcohol vapor passed through an absorption tube containing "dehydrite" and phosphorus pentoxide.

From the combustion experiments in the calorimetric reaction vessel the following data were available: (*a*) The increase in weight of the carbon dioxide absorber, (*b*) the increase in weight of the water absorber, and (*c*) the mass of alcohol (0.00058 g) that was unburned

[8] These tests were the same as those described in an earlier paper (2).

during the sparking period (five seconds). By subtracting 0.00058 g from the increase in weight of the water absorber, and converting the weights of water and carbon dioxide to vacuum, values of the ratio $\frac{2\ (\text{moles } H_2O)}{3\ (\text{moles } CO_2)}$ were obtained from seven experiments. These data are given in Table 2. From the average value of 1.00037 for this ratio, the amount of water in the alcohol is computed to be 0.043 per cent by weight. This agrees, within the experimental error, with the value obtained from the density measurements.

TABLE 2.—*Ratio of carbon to hydrogen in the ethyl alcohol*

Experiment	Mass [1] of H_2O	Mass of CO_2	$\frac{2\ (\text{moles } H_2O)}{3\ (\text{moles } CO_2)}$	Deviation from mean
	g	*g*		
X	1.64219	2.67210	1.00065	0.00028
A	1.69878	2.76374	1.00081	.00044
B	1.72781	2.81263	1.00022	−.00015
C	1.68556	2.74384	1.00023	−.00014
D	1.72177	2.80318	1.00009	−.00026
E	1.69205	2.75433	1.00025	−.00012
F	1.67569	2.72742	1.00035	−.00002
Mean [2]			1.00037	±.00020

[1] The actual increase in mass of the absorber for water was decreased by 0.00058 g to give the mass of H_2O. This is explained in the text, p. 122.

[2] Omitting the results of experiment A gives 1.00030 ±0.00015; and omitting the results of experiments A and X gives 1.00023 ±0.00006.

2. PURITY OF THE COMBUSTION REACTION

The air used to carry the alcohol vapor into the reaction vessel in the calorimeter was freed from carbon dioxide and water vapor by preliminary passage through "ascarite," "dehydrite," and phosphorus pentoxide. There was no cumbustible material in the air because, when it was passed through a tube containing palladinized asbestos at 500° C., no carbon dioxide was detected in the exit gas. The oxygen used to supply the "atmosphere" for these combustions was the same as that used in the previous investigations and was similarly purified (2).

In order to determine whether the process of bubbling air through the alcohol caused any oxidation, oxygen was passed through a sample of pure alcohol at 40° C., and the vapors were condensed to liquid at 0° C. Tests of the initial liquid and of the distillate showed the presence of only a trace (1 in 100,000) of aldehyde, both in the case of methyl alcohol and of ethyl alcohol.[9]

Examination of the gaseous products of the combustion of methyl alcohol showed the presence of a negligible amount of formaldehyde (1 mole per 800,000 moles of alcohol), and of nitrogen oxides[10] (1 mole per 40,000 to 60,000 moles of alcohol). No carbon monoxide was found in tests which would have detected 1 mole per 30,000 moles of methyl alcohol.

In the case of ethyl alcohol, examination of the gaseous products of combustion showed the presence of a negligible amount of nitrogen oxides (1 mole per 20,000 to 30,000 moles of alcohol) and a trace of carbon monoxide (1 mole per 20,000 moles of alcohol). In the liquid

[9] The procedure used in making the aldehyde tests was that described in (9).

[10] The tests for nitrogen oxides were made with the Griess reagent (fuchsin-sulphite) according to (10).

water produced in the combustion of ethyl alcohol the amount of nitric acid formed from nitrogen oxides and water was about 1 mole per 40,000 moles of alcohol, and the amount of acetic acid, if any, formed from incomplete combustion of the alcohol, was not more than 1 mole per 60,000 moles of ethyl alcohol.[11]

The heat effects accompanying these side reactions are negligible. Their effect upon the measured heat value is in some cases positive and in others negative. In the worst case the effect is about 0.005 per cent.

3. DETERMINATION OF THE AMOUNT OF REACTION

In the calorimetric combustion experiments the amount of reaction was determined from the mass of carbon dioxide formed. The procedure employed in handling and manipulating the absorbing tubes, and the method of calculating the weights to vacuum have already been described (2).

V. CALORIMETRIC APPARATUS AND PROCEDURE

The calorimetric apparatus that was assembled in this laboratory for determining heats of reaction between gases was employed in the present investigation (2), and a similar procedure was followed with regard to the calorimetric technic.

The alcohol was vaporized by passing the stream of air through a sintered glass filter placed at the bottom of a cylindrical vessel containing the pure alcohol (liquid). This saturator was immersed in water which was maintained at the temperature of the room. The air entered the bottom of the saturator, passed upward through the liquid alcohol, and was thus saturated with alcohol vapor. On leaving the saturator the combustible mixture passed first through a plug of glass wool placed beyond the upper or exit end of the saturator, and then through some 8 m of pyrex laboratory glass tubing at the room temperature before reaching the calorimeter.

For an actual calorimetric experiment the combustible gas was kept flowing into a waste tube until the time for initiating the reaction, when it was switched into the burner tube of the reaction vessel in the calorimeter simultaneously with the closing of the spark circuit, which, for uniformity, was closed for 10 seconds at the start of each methyl-alcohol experiment and for 5 seconds at the start of each ethyl-alcohol experiment. The combustible mixture thus ignited burned quietly in a blue flame at the burner tip. The oxygen "atmosphere" for the combustion was kept flowing, at a rate in excess of the amount required, into the side entrance tube of the reaction vessel from a time one minute before ignition to four or five minutes after extinction of the flame. When a sufficient amount of reaction had taken place, as evidenced by the temperature rise of the calorimeter, the flow of combustible gas into the calorimeter was stopped and oxygen was simultaneously sent down the burner tube. This latter operation served to burn up all the alcohol in the burner tube (the flame continued to burn one or two seconds after stopping the

[11] This test was made by adding a drop or two of concentrated aqueous ammonia to the liquid water formed in the combustion of 0.1 mole of ethyl alcohol, and weighing the solid residue formed upon evaporation at 80° to 90° C. This residue, 0.3 mg, was found, by means of the phenoldisulfonic acid test, to be about two-thirds ammonium nitrate, the remainder possibly being ammonium acetate.

flow of air and alcohol). Most of the water formed was condensed to liquid in the lower chamber of the reaction vessel. All of the carbon dioxide, and some water vapor, were carried out of the reaction vessel by the excess gas. On leaving the calorimeter the gas passed first through a glass U tube containing "dehydrite" (and phosphorus pentoxide), which absorbed the water, and then through a second U tube containing "ascarite" (and phosphorus pentoxide), which absorbed the carbon dioxide, and finally through a guard tube containing, in order, phosphorus pentoxide, "dehydrite," and "ascarite." When the flow of oxygen was stopped some four or five minutes after extinction of the flame, the U tubes were closed.

The experiments with methyl alcohol were performed in January and February, 1931, the room temperature being 22° to 24° C. At this temperature the combustible mixture contained about 1 mole of methyl alcohol per 6 moles of air and was fed into the reaction vessel in the calorimeter at such a rate that about 0.057 mole of methyl alcohol was consumed in 30 to 32 minutes.

In order to burn ethyl alcohol in the same burner tube and at about the same rate of heat evolution, it became necessary to have a higher concentration of ethyl-alcohol vapor in the air-alcohol mixture than could be obtained at a room temperature of 22° to 24° C. The ethyl-alcohol experiments were carried out in August, 1931, when the temperature of the laboratory room was kept at 32° to 33° C. At this temperature, air saturated with ethyl alcohol formed a combustible mixture which was ignited more easily, under the given conditions, than air saturated with methyl-alcohol vapor at 22° to 24° C. At 32° to 33° C. the mixture of air and ethyl alcohol contained about 1 mole of alcohol per 8 moles of air, and was burned at such a rate that about 0.031 mole of ethyl alcohol was consumed in 22 to 23 minutes.[12]

As finally carried out, the combustions of methyl alcohol were initiated with a sparking period of 10 seconds, while a sparking period of 5 seconds was more than ample to start the combustion of the ethyl alcohol. Both these periods were in excess of the time that was actually required, on the average, for the particular conditions of the experiments, but it was deemed wise to continue the sparking for several seconds longer than necessary in order not to jeopardize the successful initiation of any given combustion experiment. The only evidence given to the operator to decide whether the combustible mixture had been properly ignited was the beginning of the sharp temperature rise in the calorimeter, which occurred about 20 seconds after the combustion began.

Because the gas which was fed into the burner tube of the reaction vessel in the alcohol experiments was a combustible mixture, a necessary change was made in the arrangement of the sparking lead running down the burner tube. Inspection of Figure 1 shows that the continuity of the two sparking leads is broken with a gap at their entrance into the reaction vessel. In the present experiments it was necessary to prevent contact of the sparks with the combustible gas before it reached the burner tip. This was accomplished by covering

[12] The early attempts (February, 1931) to burn a mixture containing about 1 mole of ethyl alcohol per 14 moles of air (the mixture which would be obtained with a room temperature of 22° C.) were unsuccessful because the flame tended to blow off this particular burner tip, even when the rate of flow was greatly reduced and when oxygen was used as a carrier. In a preliminary experiment with methyl alcohol, using oxygen as a carrier, the velocity of flow of the combustible mixture fell below the flame velocity, with the result that the flame traveled back through the combustible mixture.

the gap in the spark lead in the burner tube with a piece of capillary glass tubing, the discontinuity of the platinum wire being preserved.

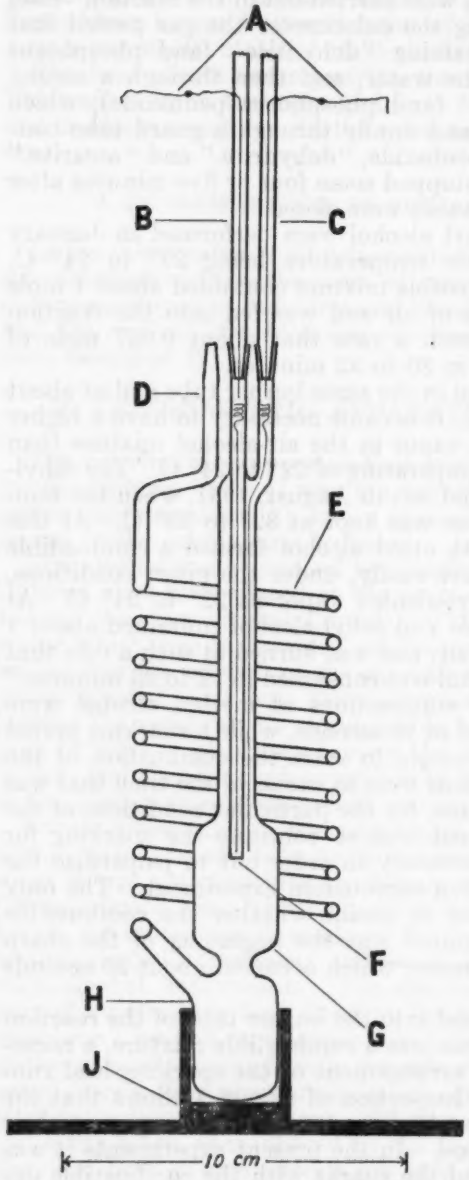

FIGURE 1.—*Cross section of the reaction vessel and supporting frame*

A, leads of spark circuit; *B*, *C*, inlet tubes; *D*, exit tube; *E*, cooling coil; *F*, burner tube; *G*, reaction chamber; *H*, condensing chamber; *J*, supporting frame

In some of the trial combustions with methyl alcohol the combustible mixture reacted on the surface of the platinum wire running down the burner tube and prevented the maintenance of a flame at the tip. This preliminary reaction was stopped by covering the lower three-fourths of the platinum lead with capillary glass tubing.

The difference in temperature between the calorimeter water and the gases issuing from the cooling coil of the reaction vessel during a combustion was found, by measurement with a single junction thermoelement made of No. 36 constantan and copper wires, to be zero within 0.05° C. If all the issuing gases left at a temperature 0.05° C. higher than the calorimeter water, the amount of energy lost would be 1 part in 100,000 of the total.

A new heater for imparting electrical energy to the calorimeter was built and used in the present experiments. This heater was made by winding, noninductively, No. 30, B. & S. gage, enameled constantan wire around a cylindrical piece of pyrex laboratory glass tubing, 1¼ inches in diameter and 2 inches long, and covering the layer of wire with "pizein," a black tarlike cement having a low melting temperature and high insulation resistance, and which is insoluble in water. Enameled copper leads (No. 24, B. & S. gage) were soldered to the ends of the constantan wire and insulated with "pizein" on the glass form. The potential leads (No. 28, B. & S. gage, enameled copper) were soldered to the current leads midway in the air gap between the

calorimeter can and the jacket, and all four leads were imbedded in deKhotinsky wax which was firmly cemented to the jacket. The resistance of the heater was about 66 ohms. The amount of water absorbed by this "pizein" was found to be practically zero (±3 mg) in an experiment in which about 5 g of the material, cut up into small pieces, was immersed in boiling water for two hours and in water at room temperature for several months. In all the experiments the heater was slipped down over the central part of the reaction vessel where it surrounded the reaction chamber.

VI. CALORIMETRIC DATA ON METHYL ALCOHOL

1. CORRECTION EXPERIMENTS

In order to determine the energy introduced into the calorimeter by the igniting operation, three experiments were made, in each of which there were two separate ignitions and extinctions of the flame, which was permitted to burn several seconds after the spark circuit was broken.

The results of the "correction" experiments are given in Table 3, the column headings of which are self-explanatory. In these experiments the amount of alcohol burned was small, and all of the water formed was carried out of the calorimeter as vapor. The method of computing the "gas" and the "vaporization" values is explained in the previous paper (2).

TABLE 3.—*Correction experiments (for methyl alcohol)*

No.	Electrical equivalent of calorimeter	Δt_{corr}	Total energy	"Gas" energy	"Vaporization" energy	Heat of combustion of CH_3OH	Total ignition energy	Number of ignitions (10 seconds each)	"Spark" energy for each period of 10 seconds
	Joules °*C.*$^{-1}$	°*C.*	*Joules*	*Joules*	*Joules*	*Joules*	*Joules*		*Joules*
α	1.5554	0.01505	234.1	4.5	24.4	211.6	51.4	2	25.7
β	1.5619	.01275	199.1	3.7	19.8	172.6	50.0	2	25.0
γ	1.5528	.01396	208.5	0.1	20.1	175.0	53.7	2	26.9
Mean									25.9

2. ELECTRICAL ENERGY EXPERIMENTS

The results of the experiments of the methyl alcohol group to determine the electrical energy equivalent of the calorimeter are given in Table 4. The symbols heading the various columns have already been defined (2). These data determined the electrical energy equivalent of the calorimeter for the particular conditions existing at the time of the methyl alcohol experiments.

3. COMBUSTION EXPERIMENTS

The data of the 10 calorimetric experiments in which methyl alcohol was burned in the calorimeter are given in Table 5.

TABLE 4.—*Electrical energy experiments (for methyl alcohol)*

Experiment No.	ΔR	k	u	K	U	$\Delta R_{corr.}$
	Ohm	*Min*$^{-1}$	*Ohm min*$^{-1}$	*Ohm*	*Ohm*	*Ohm*
1	0.290818	0.001851	−0.0000004	0.007989	0.0000160	0.282845
2	.291063	.001840	.0000080	.008435	.000320	.282328
3	.289821	.001844	.0000090	.008556	.000360	.280905
4	.290390	.001854	.0000074	.008321	.000296	.281773

Experiment No.	$\Delta t_{corr.}$	Average temperature [1]	Electrical energy [2]	Mass of calorimeter water	Electrical equivalent of calorimeter system [3]	Deviation from mean
	°*C.*	°*C.*	*Int. joules*	*g*	*Int. joules* °*C.*$^{-1}$	*Joules* °*C.*$^{-1}$
1	2.80386	25.13	43,479.1	3,635.90	15,566.0	0.2
2	2.79868	25.06	43,386.2	3,634.56	15,567.0	1.2
3	2.78457	25.05	43,368.6	3,652.17	15,565.6	−.2
4	2.79318	25.06	43,065.5	3,614.93	15,564.7	−1.1
Mean					15,565.8	±.7

[1] The room temperature was 22° to 24° C.
[2] The time of electrical energy input was 1,800.00 seconds.
[3] Corrected to 3,650.00 g of water and an average temperature of 25.00° C.

TABLE 5.—*Reaction experiments (combustion of gaseous methyl alcohol)*

Experiment	ΔR	k	u	K	U	$\Delta R_{corr.}$	$\Delta t_{corr.}$	Average temperature [1]
	Ohm	*Min*$^{-1}$	*Ohm min*$^{-1}$	*Ohm*	*Ohm*	*Ohm*	°*C.*	°*C.*
A	0.285721	0.001818	0.0000144	0.008348	0.000576	0.276797	2.74385	25.07
B	.205545	.001815	.0000225	.010992	.000900	.193617	1.91909	24.66
C	.290942	.001833	.0000091	.008527	.000364	.282051	2.79593	25.06
D	.286678	.001837	−.0000021	.008494	−.000084	.278268	2.75843	25.06
E	.287472	.001823	.0000084	.008473	.000336	.278663	2.76234	25.04
F	.289998	.001808	.0000149	.008715	.000596	.280687	2.78241	25.06
G	.290717	.001827	.0000013	.008660	.000052	.282005	2.79545	25.02
H	.288422	.001845	.0000040	.009432	.000160	.278830	2.76398	25.02
I	.291813	.001885	.0000042	.008829	.000168	.282816	2.80352	25.07
J	.291169	.001848	.0000030	.008523	.000120	.282526	2.80064	25.06

Experiment	Mass of calorimeter water	Electrical equivalent of calorimeter system	Total energy [2]	"Gas" energy	"Vaporization" energy	"Spark" energy	Mass of CO_2 formed	$Q_{25°\,C.,\,1\,atm.}$	Deviation from mean
	g	*Int. joules* °*C.*$^{-1}$	*Int. joules*	*Joules*	*Int. joules*	*Joules*	*Mole*	*Int. kilojoules mole*$^{-1}$	*Kilojoules mole*$^{-1}$
A	3,640.51	15,530.1	42,612.3	7.5	515.8	25.9	0.056468	763.44	−0.24
B	3,659.03	15,606.7	29,950.7	30.1	441.9	25.9	.039796	763.82	.14
C	3,657.02	15,599.0	43,613.7	23.9	461.9	25.9	.057763	(763.01)	
D	3,651.38	15,575.2	42,963.1	16.1	616.1	25.9	.057042	763.81	.13
E	3,654.07	15,586.6	43,055.5	29.5	543.4	25.9	.057699	763.63	−.05
F	3,651.72	15,576.7	43,340.8	16.0	544.6	25.9	.057442	763.82	.14
G	3,644.11	15,545.0	43,455.3	22.5	539.5	25.9	.057615	763.54	−.14
H	3,643.91	15,544.1	42,963.6	38.7	621.0	25.9	.057081	763.78	.10
I	3,634.70	15,505.6	43,470.3	36.5	615.8	25.9	.057760	763.45	−.23
J	3,617.11	15,432.1	43,219.8	15.5	584.9	25.9	.057335	763.83	.15
Mean [3]								763.68	±.15

[1] The room temperature was 22° to 24° C.
[2] The time of reaction was 30 to 31 minutes.
[3] The result of experiment C is not included.

The "vaporization" energy was equal to the heat of vaporization of that mass of water, m_v, formed in the combustion, which was not condensed to liquid during the calorimetric experiment. The increase in mass of the solid absorbent in the first U tube was not exactly equal to m_v because first, the alcohol itself might contain water, and second, a small amount of alcohol vapor (<2 mg) came through unburned at the beginning of each combustion experiment and was completely absorbed in the "dehydrite." The method of determining m_v in the methyl-alcohol experiments is as follows:

m_a is the mass of the solid absorbent in the first U tube at the beginning of the calorimetric experiment.

m_b is the mass of water which was contained as vapor in the reaction vessel at the conclusion of the calorimetric experiment.

m_c is the mass of unburned alcohol which was absorbed in the first U tube.

m_d is the mass of water contained in the alcohol vapor consumed in the given experiment.

n is the number of moles of carbon dioxide formed in the experiment.

m_e is the mass of the solid absorbent in the first U tube at the end of the calorimetric experiment.

m_f is the mass of the solid absorbent in the first U tube after all the water has been carried from the reaction vessel into the first U tube.

M_w is the molecular weight of water.

The quantities determined experimentally are m_a, m_b, m_e, m_f, and n. These are related by the following equations:

$$m_e - m_a = m_v - m_b + (m_c + m_d)$$

$$m_f - m_a = 2nM_w + (m_c + m_d)$$

Therefore

$$m_v = m_e - m_f + m_b + 2nM_w$$

In the present method, the amount of water contained in the alcohol is not involved in the calorimetric calculation.

4. RESULTS OF THE PRESENT WORK

From the data of the present experiments, the heat evolved in the reaction

$$CH_3OH_{(g)} + 3/2O_{2(g)} = CO_{2(g)} + 2H_2O_{(l)} \qquad (1)$$

at 25° C. and a constant total pressure of 1 atmosphere, with the alcohol near saturation pressure, is found to be 763.68 international kilojoules per mole of methyl alcohol. The average deviation for the 10 experiments was ±0.15 kilojoule per mole. The preliminary value previously reported (11) for the heat of the above reaction was given as 763.77, but this included a wrong pressure correction (12). The value 763.68 is the one which is correctly obtained from the present data.

For the group of experiments on methyl alcohol, the "error" (2), $\pm 2\sqrt{\frac{\Sigma(x-\bar{x})^2}{n(n-1)}}$, is equal to ±0.007 per cent for the electrical energy experiments, and to ±0.015 per cent for the combustion experiments. The "combined error," taken as the square root of the sum of the

squares of the two percentage errors, is ±0.017 per cent, or ±0.13 kilojoule per mole. The value given for the heat of combustion of methyl alcohol is conservatively estimated to be reliable within ±0.20 kilojoule per mole. The heat of demixing air and alcohol vapor is considered negligible.

From the data of Fiock, Ginnings, and Holton (3), the heat evolved in the process

$$CH_3OH_{(l)} = CH_3OH_{(g)} \quad (2)$$

at 25° C. and saturation pressure is

$$Q = -37.43 \pm 0.03 \text{ international kilojoules per mole}$$

Addition of equations (1) and (2) gives for the reaction

$$CH_3OH_{(l)} + 3/2O_{2(g)} = CO_{2(g)} + 2H_2O_{(l)} \quad (3)$$

at 25° C. and a constant pressure of 1 atmosphere

$$Q = 726.25 \pm 0.20 \text{ international kilojoules per mole}$$

The change in heat content of the liquid from saturation pressure to 1 atmosphere is negligible.

5. DATA OF PREVIOUS INVESTIGATORS

The heat of combustion of methyl alcohol has been the subject of experiments reported by Favre and Silbermann (13) in 1852; Thomsen (14) in 1880; Stohmann, Kleber, and Langbein (15) in 1889; Richards and Davis (16) in 1920; Roth and Müller (17) in 1927; and Roth and Banse (18), and the I. G. Farbenfabrik (18), in 1931. All of these investigators employed the bomb method, except Favre and Silbermann, and Thomsen, who burned the alcohol in a flame at constant pressure.

Favre and Silbermann (13) had not the advantages of modern calorimetric technic nor of pure material to work with, so their results have only a historical interest.

Thomsen (14), by sending the vapor of methyl alcohol at its boiling point into the calorimeter to be burned in oxygen at constant pressure, measured, for the heat evolved in the reaction,

$$CH_3OH_{(g,\ 65°\ C.)} + 3/2\ O_{2(g,\ 18°\ C.)} = CO_{2(g,\ 18°\ C.)} + 2H_2O_{(l,\ 18°\ C.)} \quad (4)$$

$$Q = 182.92 \text{ kg-cal}_{18} \text{ per mole}$$

This was the average of eight experiments. The data on the heat content and the heat of vaporization of methyl alcohol, which were obtained by Fiock, Ginnings, and Holton (3), can be combined with the data of Thomsen to give the heat of combustion of liquid methyl alcohol at 18° C. For the process

$$CH_3OH_{(l,\ 65°\ C.)} = CH_3OH_{(g,\ 65°\ C.)} \quad (5)$$

$$Q = -35.23 \text{ international kilojoules per mole}$$

and for

$$CH_3OH_{(l,\ 18°\ C.)} = CH_3OH_{(l,\ 65°\ C.)} \quad (6)$$

$$Q = -3.95 \text{ kilojoules per mole}$$

Conversion of kg-cal.$_{18}$ to international kilojoules, and addition of these equations, give for the heat of combustion of liquid methyl alcohol at 18° C., the value 725.44. For the reaction at 25° C., this becomes 725.2 international kilojoules per mole. The "error," estimated by the present author, is ±1.6 kilojoules per mole. The data which Thomsen obtained by his "universal burner" method has been subject to the criticism that the results obtained are too high because of an unaccounted-for flow of heat from the boiler to the calorimeter, the higher boiling liquids giving increasingly too high results.

Stohmann, Kleber, and Langbein (15), in carrying out their experiments, placed the alcohol in the bomb in a sealed glass bulb. After oxygen to the desired pressure had been added, the glass bulb was broken by shaking the bomb. Before the actual calorimetric experiment was begun, then, the interior of the bomb was saturated with alcohol vapor, the heat of vaporization of which was properly accounted for. According to Richards and Jesse (19) the method used by Stohmann for burning volatile liquids leads to incomplete combustion and consequent low results. From the data of six experiments, Stohmann, Kleber, and Langbein give an average value of 5.3215 kg-cal.$_{15}$ per g of alcohol (weighed in air?) at constant volume in the bomb, the final temperature of the calorimeter being about 18° C. Converted to international kilojoules per mole at 25° C. and constant pressure, the value becomes 714. The estimated "error" is ±2 kilojoules per mole.

Richards and Davis (16) performed five experiments by burning methyl alcohol in a bomb at constant volume, using accurate calorimetric technic and an improved method of placing the liquid alcohol in a glass bulb in the bomb, the tip of the bulb being broken at the time of ignition. Although this procedure worked admirably well for the higher boiling liquids with which they experimented, Richards and Davis reported for methyl alcohol, that "The combustions with this substance were the least satisfactory, perhaps because of its volatility. Unfortunately only one could be analyzed for carbon monoxide, because of lack of time." In this one experiment quite an appreciable amount of carbon monoxide was found, the heat correction being about one-fourth per cent. Richards and Davis gave the density of the methyl alcohol burned by them as $d_4^{20}=0.7923$. This value is 0.12 per cent higher than the present "best" value (7). If the increased density were due to water, then the value for the heat of combustion of methyl alcohol from these data would be too low by a percentage amount corresponding to the weight per cent of water present. Richards and Davis reported for the heat of combustion of liquid methyl alcohol in their bomb at constant volume, the value 5.333 kg-cal.$_{18}$ per g (weighed in air) at 20° C. Converted to international kilojoules, the heat of combustion at 25° C. and constant pressure becomes 714.2 international kilojoules per mole. The estimated "error" is ±2 kilojoules per mole.

The details of the experiments performed by Roth and Müller (17), Roth and Banse (18), and the I. G. Farbenfabrik (18), have not been published, but the values are reported in the Landolt-Börntsein-Roth-Scheel tables. Roth and Müller give 5.365, Roth and Banse 5.431, and the I. G. Farbenfabrik 5.423, kg-cal.$_{15}$ per g of methyl alcohol (weighed in air) at 20° C. and constant volume. When converted to

international kilojoules per mole at 25° C. and constant pressure, these values become 719, 727.8, and 726.7, respectively. Roth and Banse have recalculated their value since its appearance in the Landolt-Börnstein-Roth-Scheel tables, and in a private communication to the present author give the value 5.418 kg-cal.$_{15}$ per g (weighed in air) at 20° C. and constant volume. Their corrected value becomes 726 international kilojoules per mole at 25° C. and a constant pressure of 1 atmosphere.

In Figure 2 are plotted the results of the foregoing investigations on methyl alcohol, together with that of the present work.

VII. CALORIMETRIC DATA ON ETHYL ALCOHOL

1. CORRECTION EXPERIMENTS

The energy introduced into the calorimeter by the igniting operation was determined from one calorimetric experiment which consisted of six separate ignitions and extinctions of the flame. These data are given in Table 6.

TABLE 6.—*Correction experiments (for ethyl alcohol)*

No.	Electrical equivalent of calorimeter	$\Delta t_{corr.}$	Total energy	"Gas" energy	"Vaporization" energy	Heat of combustion of C_2H_5OH	Total ignition energy	Number of ignitions (5 seconds each)	"Spark" energy for each period of 5 seconds
	Joules °*C*$^{-1}$	° *C.*	*Joules*	*Joules*	*Joules*	*Joules*	*Joules*		*Joules*
a	15,420.0	0.05181	798.9	4.7	77.7	836.9	44.4	6	7.4

2. ELECTRICAL ENERGY EXPERIMENTS

The electrical energy equivalent of the calorimeter for the conditions prevailing at the time of the ethyl alcohol experiments was determined from the data given in Table 7.

TABLE 7.—*Electrical energy experiments (for ethyl alcohol)*

Experiment No.	ΔR	k	u	K	U	$\Delta R_{corr.}$
	Ohms	*Min.*$^{-1}$	*Ohm min.*$^{-1}$	*Ohm*	*Ohm*	*Ohm*
1	0.289065	0.001946	0.0000017	0.007163	0.000051	0.281851
2	.288833	.001966	.0000139	.007066	.000417	.281350
3	.288994	.001969	.0000091	.007094	.000273	.281627
4	.288195	.001980	.0000044	.007086	.000132	.280977
5	.288267	.001972	.0000035	.007157	.000105	.281110

Experiment No.	$\Delta t_{corr.}$	Average temperature [1]	Electrical energy [2]	Mass of calorimeter water	Electrical equivalent of calorimeter system [3]	Deviation from mean
	° *C.*	° *C.*	*Int. joules*	*g*	*Int. joules* °*C.*$^{-1}$	
1	2.80011	32.51	43386.1	3633.12	15481.4	2.9
2	2.79514	32.52	43301.3	3632.55	15481.0	2.5
3	2.79789	32.52	43311.5	3630.70	15477.2	−1.3
4	2.79143	32.52	43210.1	3630.80	15476.3	−2.2
5	2.79275	32.52	43210.6	3629.05	15476.4	−2.1
Mean					15478.5	±2.2

[1] The room temperature was 32° to 33° C.
[2] In each experiment the time of electrical energy input was 1,380.00 seconds.
[3] Corrected to 3,630 g water and an average temperature of 32.50° C.

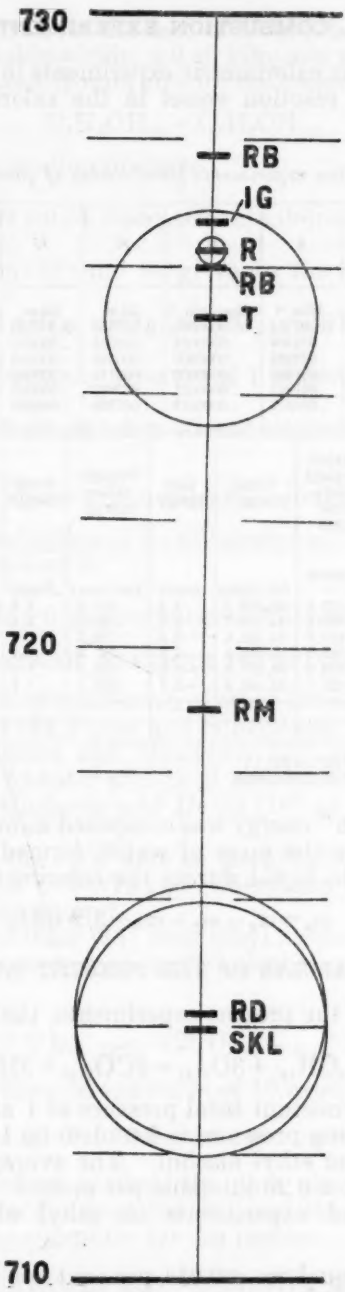

FIGURE 2.—*Plot of the data on methyl alcohol*

The ordinate scale gives the heat of combustion of liquid methyl alcohol at 25° C. and a constant pressure of 1 atmosphere, in international kilojoules per mole. The circles measure the assigned "error" of the respective average values which are indicated for the following investigations: *SKL*, Stohmann, Kleber, and Langbein; *IG*, I. G. Farbenfabrik; *RD*, Richards and Davis; *RB*, Roth and Banse; *RM*, Roth and Müller; *T*, Thomsen; *R*, Rossini.

3. COMBUSTION EXPERIMENTS

The data of the six calorimetric experiments in which ethyl alcohol was burned in the reaction vessel in the calorimeter are given in Table 8.

TABLE 8.—*Reaction experiments (combustion of gaseous ethyl alcohol)*

Experiment No.	ΔR	k	u	K	U	$\Delta R_{corr.}$	$\Delta t_{corr.}$	Average temperature [1]
	Ohm	*Min.*$^{-1}$	*Ohm min.*$^{-1}$	*Ohm*	*Ohm*	*Ohm*	°*C.*	°*C.*
A	0.286865	0.001984	0.0000064	0.007385	0.000230	0.279250	2.77427	32.52
B	.293712	.001969	.0000024	.006585	.000086	.287041	2.85167	32.52
C	.287405	.001985	.0000069	.006360	.000248	.280797	2.78967	32.52
D	.293056	.001980	.0000000	.006743	.000000	.286313	2.84447	32.54
E	.288895	.001982	.0000027	.007692	.000097	.281106	2.79271	32.52
F	.287143	.001981	.0000019	.007388	.000068	.279687	2.77861	32.51

Experiment No.	Mass of calorimeter water	Electrical equivalent of calorimetric system	Total energy [2]	Gas energy	Vaporization energy	Spark energy	One-half mass of CO_2 formed	$Q_{25.5°\,C.,\,1\,atm.}$	Deviation from mean
	g	*Int. joules* °*C.*$^{-1}$	*Int. joules*	*Joules*	*Int. joules*	*Joules*	*Mole*	*Int. joules mole*$^{-1}$	
A	3,664.62	15,625.8	43,350.2	3.4	854.5	7.4	0.0314062	1,407.39	−0.09
B	3,636.01	15,506.6	44,219.7	2.2	785.6	7.4	.0319617	1,407.94	.44
C	3,624.31	15,457.6	43,121.6	−0.5	765.7	7.4	.0311800	1,407.29	−.21
D	3,630.86	15,485.0	44,046.6	1.6	797.3	7.4	.0318543	1,407.80	.30
E	3,633.59	15,496.4	43,277.0	−2.2	778.0	7.4	.0312992	1,407.24	−.26
F	3,616.19	15,423.7	42,856.4	−2.1	771.4	7.4	.0309934	1,407.34	−.13
Mean								1,407.50	±.26

[1] The room temperature was 32° to 33° C.
[2] The time of reaction was 22 to 23 minutes.

The "vaporization" energy was computed as for the methyl alcohol experiments.[13] Here the mass of water, formed in the combustion, but not condensed to liquid during the calorimetric experiment, was

$$m_g = m_e - m_f + m_b + 3/2\ nM_w$$

4. RESULTS OF THE PRESENT WORK

From the data of the present experiments, the heat evolved in the reaction

$$C_2H_5OH_{(g)} + 3O_{2(g)} = 2CO_{2(g)} + 3H_2O_{(l)} \qquad (7)$$

at 32.50° C. and a constant total pressure of 1 atmosphere, with the alcohol near saturation pressure, is found to be 1407.50 international kilojoules per mole of ethyl alcohol. The average deviation for the six experiments was ±0.26 kilojoule per mole.

For the group of experiments on ethyl alcohol the "error," $\pm 2\sqrt{\frac{\Sigma(x-\bar{x})^2}{n(n-1)}}$, is equal to ±0.014 per cent for the electrical energy experiments and to ±0.017 per cent for the combustion experiments. The "combined error" is ±0.022 per cent, or ±0.31 kilojoule per

[13] See p. 129.

mole. The value given for the heat of combustion of ethyl alcohol is estimated to be reliable within ± 0.40 kilojoule per mole.

Fiock, Ginnings, and Holton give for the heat evolved in the process

$$C_2H_5OH_{(l)} = C_2H_5OH_{(g)} \quad (8)$$

at 32.50° C. and saturation pressure

$$Q = -41.92 \pm 0.04 \text{ international kilojoules per mole}$$

Addition of equations (7) and (8) gives for the reaction

$$C_2H_5OH_{(l)} + 3O_{2(g)} = 2CO_{2(g)} + 3H_2O_{(l)} \quad (9)$$

at 32.50° C. and a constant pressure of 1 atmosphere

$$Q = 1365.58 \pm 0.40 \text{ international kilojoules per mole}$$

Since $\Delta C_p\left(- = \frac{dQ}{dT}\right)$ for reaction (9) is 97.3 joules per mole per degree, then the heat of combustion of liquid alcohol at 25° C. and a constant pressure of 1 atmosphere is

$$Q = 1366.31 \pm 0.40 \text{ international kilojoules per mole}$$

5. DATA OF PREVIOUS INVESTIGATORS

Values for the heat of combusion of ethyl alcohol have been reported by Andrews (20) in 1848, Favre and Silbermann (13) in 1852, Thomsen (14) in 1880, Berthelot and Matignon (21) in 1892, Atwater and Rosa (22) in 1899, Atwater and Snell (23) in 1903, Emery and Benedict (24) in 1911, Richards and Davis (16) in 1920, and Roth and Müller (17) in 1927.

As in the case of the early date on methyl alcohol, the experiments of Andrews (20), and of Favre and Silbermann (13), on ethyl alcohol are only of historical interest.

Thomsen's experiments (14) with ethyl alcohol were carried out in a manner similar to those with methyl alcohol. For the heat evolved in the reaction

$$C_2H_5OH_{(g,\,78°C.)} + 3O_{2(g,\,18°C.)} = 2CO_{2(g,\,18°C.)} + 3H_2O_{(l,\,18°C.)} \quad (10)$$

Thomsen reported the average value of 10 experiments to be

$$Q = 341.79 \text{ kg-cal}_{18} \text{ per mole}$$

Utilizing, as for methyl alcohol, the data obtained by Fiock, Ginnings and Holton on the heat content and the heat of vaporization of ethyl alcohol, one computes for the process

$$C_2H_5OH_{(l,\,78°C.)} = C_2H_5OH_{(g,\,78°C.)} \quad (11)$$

$$Q = -38.72 \text{ international kilojoules per mole}$$

and for

$$C_2H_5OH_{(l,\,18°C.)} = C_2H_5OH_{(l,\,78°C.)} \quad (12)$$

$$Q = -7.37 \text{ kilojoules per mole}$$

Then, from these data, the heat of combustion of liquid ethyl alcohol at 18° C. becomes 1,382.6 international kilojoules per mole. For the reaction at 25° C., the value reduces to 1,381.9. The estimated "error" is ± 2.2 kilojoules per mole.

Berthelot and Matignon (21) performed two experiments by absorbing the ethyl alcohol in pellets of cellulose and burning these in their bomb at constant volume. The data of these investigators appear to give the value 7.068 kg-cal_{13} for the heat of combustion of 1 g of ethyl alcohol (weighed in air?) at 14° C. and constant volume. Converted to international kilojoules per mole at 25° C. and constant pressure, this value becomes 1,362. The "error" of this value is taken as ± 4 kilojoules per mole.

Atwater and Rosa (22) reported the results of 20 experiments in which alcohol containing about 10 per cent of water was burned in a bomb at constant volume—in some experiments the alcohol was absorbed in cellulose filter blocks and in others gelatin capsules were used to contain the alcohol before it was placed in the bomb. The percentage content of alcohol was determined from the density of the various samples. The average of these experiments was 7.067 kg-cal_{20} per g of ethyl alcohol (weighed in air) at 20° C. and constant volume. This value should be increased by 0.02 per cent because of the heat effect of diluting the alcohol with water. Converted to 25° C. and constant pressure, these data give for the heat of combustion of liquid ethyl alcohol the value 1,360 international kilojoules per mole. The estimated "error" is ± 4 kilojoules per mole.

Atwater and Snell (23) reported, without detail, the results of six experiments on the combustion of ethyl alcohol in their bomb at constant volume. Their data, corrected to 25° C. and constant pressure, in international kilojoules per mole, give the value 1,363. The estimated "error" of this value is ± 4 kilojoules per mole.

Atwater and Snell also reported (23), without detail, the results of 11 series of experiments made at constant pressure in the respiration calorimeter of Atwater and Rosa (22). From their figures, the heat of combustion of liquid ethyl alcohol at 25° C. and constant pressure becomes 1,361 international kilojoules per mole, with an estimated "error" of ± 5 kilojoules per mole.

Richards and Davis (16) gave the results of four experiments performed with the calorimetric apparatus and procedure used with methyl alcohol. The average value was 7.110 kg-$cal._{18}$ per g of ethyl alcohol (weighed in air) at 20° C. and constant volume. When corrected to 25° C. and constant pressure, and to international kilojoules, this value becomes 1,368.4 international kilojoules per mole. The estimated "error" is ± 1.8 kilojoules per mole.

Emery and Benedict (24) report, without experimental details, the value 7.104 kg-$cal._{20}$ per g (weighed in air) of ethyl alcohol, for 20° C. and constant pressure. Their calorimeter was calibrated with benzoic acid, using the value 6.333 kg-$cal._{20}$ per g as its heat of combustion at constant volume. Substituting Dickinson's value (25) for benzoic acid gives 1,364 international kilojoules per mole at 25° C. and a constant pressure of 1 atmosphere.

The details of the experiments by Roth and Müller (17) are unpublished. They give the value 7.140 kg-$cal._{15}$ for the heat of combustion of 1 g of ethyl alcohol (weighed in air) at 20° C. and constant

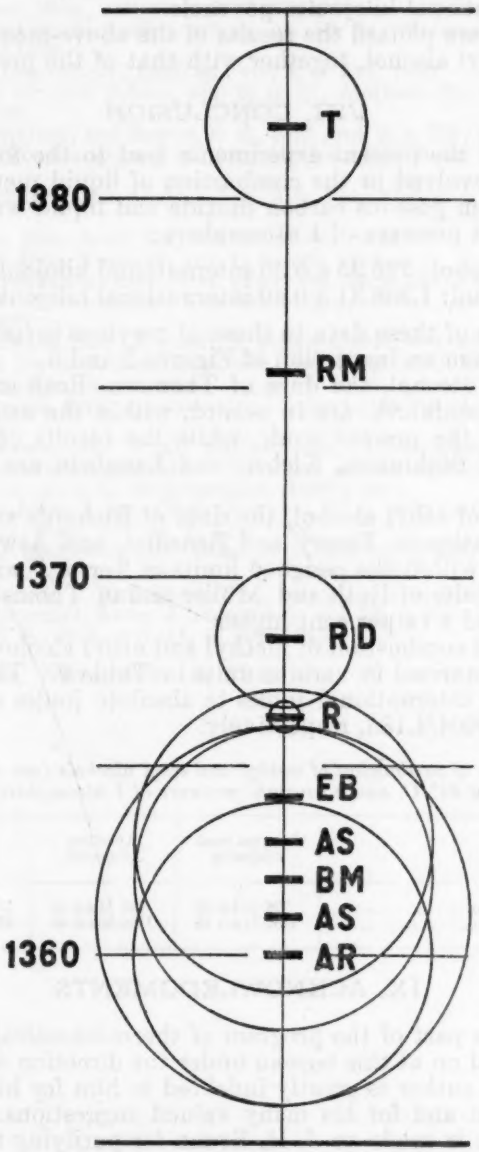

FIGURE 3.—*Plot of the data on ethyl alcohol*

The ordinate scale gives the heat of combustion of liquid ethyl alcohol at 25° C. and a constant pressure of 1 atmosphere, in international kilojoules per mole. The circles measure the assigned "error" of the respective average values which are given for the following investigations: *AR*, Atwater and Rosa; *AS*, Atwater and Snell; *BM*, Berthelot and Matignon; *EB*, Emery and Benedict; *RD*, Richards and Davis; *RM*, Roth and Müller; *T*, Thomsen; *R*, Rossini.

volume. This gives, for 25° C. and constant pressure, the value 1,375.4 international kilojoules per mole.

In Figure 3 are plotted the results of the above-mentioned investigations on ethyl alcohol, together with that of the present work.

VIII. CONCLUSION

The data of the present experiments lead to the following values for the heats evolved in the combustion of liquid methyl and ethyl alcohols to form gaseous carbon dioxide and liquid water at 25° C. and a constant pressure of 1 atmosphere:

Methyl alcohol: 726.25 ± 0.20 international kilojoules per mole
Ethyl alcohol: 1,366.31 ± 0.40 international kilojoules per mole

The relation of these data to those of previous investigators can be readily seen from an inspection of Figures 2 and 3.

For methyl alcohol, the data of Thomsen, Roth and Banse, and the I. G. Farbenfabrik, are in accord, within the assigned limits of "error," with the present work, while the results of Richards and Davis, and of Stohmann, Kleber, and Langbein are about 1.7 per cent lower.

In the case of ethyl alcohol, the data of Richards and Davis, Berthelot and Matignon, Emery and Benedict, and Atwater and Snell are in accord, within the assigned limits of "error," with the present data. The results of Roth and Müller and of Thomsen are, respectively, 0.67 and 1.14 per cent higher.

The heats of combustion of methyl and ethyl alcohols in the liquid state are summarized in various units in Table 9. The factors used for converting international joules to absolute joules and g-cal.$_{15}$ are 1.0004 and 1.0004/4.185, respectively.

TABLE 9.—*Heats of combustion of methyl and ethyl alcohols (per mole of the liquid, at 25° C. and a constant pressure of 1 atmosphere)*

	International kilojoules	Absolute kilojoules	Kg-cal.$_{15}$
$CH_3OH_{(l)}$	726.25±0.20	726.54±0.20	173.61±0.05
$C_2H_5OH_{(l)}$	1366.31±0.40	1366.86±0.40	326.61±0.10

IX. ACKNOWLEDGMENTS

This work is part of the program of thermochemical research that is being carried on at this bureau under the direction of E. W. Washburn, and the author is greatly indebted to him for his deep interest in the problem and for his many valued suggestions. Grateful acknowledgment is made to J. H. Bruun for purifying the alcohols, to the gas chemistry section of this bureau for developing the flame technic and for making the carbon monoxide tests, and to the chemical reagents laboratory of this bureau for performing the test for nitric acid.

X. BIBLIOGRAPHY

1. Giauque, J. Am. Chem. Soc., vol 52, pp. 4808, 4816; 1930; vol. 53, p. 507; 1931.
2. Rossini, B. S. Jour. Research, vol. 6, pp. 1, 37; 1931.
3. Fiock, Ginnings, and Holton, B. S. Jour. Research, vol. 6, p. 881; 1931.

4. Baxter, Curie, Hönigschmid, LeBeau, and Meyer. First Report of the Committee on Atomic Weights of the International Union of Chemistry, J. Am. Chem. Soc., vol. 53, p. 1627; 1931.
5. International Critical Tables, vol. 5, pp. 80, 81, McGraw-Hill Book Co., New York; 1929.
6. Bruun, Ind. Eng. Chem., anal. ed., vol. 1, p. 212; 1929.
7. International Critical Tables, vol. 3, p. 27, McGraw-Hill Book Co., New York; 1928.
8. Osborne, McKelvey, and Bearce, B. S., Bull., vol. 9, p. 327; 1913.
9. Woodman, "Food analysis," p. 496, McGraw-Hill Book Co., New York; 1924.
10. Lunge, "Technical Gas Analysis," p. 316, Van Nostrand Co., New York; 1914.
11. Rossini, Proc. Nat. Acad. Sci., vol. 17, p. 343; 1931.
12. Rossini, B. S. Jour. Research, vol. 7, p. 329; 1931.
13. Favre and Silbermann, Ann. chim. phys., vol. 34, p. 357; 1852.
14. Thomsen, "Thermochemische Untersuchungen," vol. 4, pp. 157–159, Barth, Leipzig; 1886.
15. Stohmann, Kleber, and Langbein, J. prakt. Chem., vol. 40, p. 341; 1889.
16. Richards and Davis, J. Am. Chem. Soc., vol. 42, p. 1599; 1920.
17. Roth and Müller, unpublished. Quoted from Landolt-Börnstein-Roth-Scheel Tabellen, first supplementary volume to the 5th ed., p. 868, Springer, Berlin; 1927.
18. Roth and Banse, and I. G. Farbenfabrik, unpublished. Quoted from Landolt-Börnstein-Roth-Scheel Tabellen, second supplementary volume to the 5th ed., pt. 2, p. 1636, Springer, Berlin; 1931.
19. Richards and Jesse, J. Am. Chem. Soc., vol. 32, p. 268; 1910.
20. Andrews, Phil. Mag., vol. 32, p. 321; 1848.
21. Berthelot and Matignon, Ann. chim. phys., vol. 27, p. 310; 1892.
22. Atwater and Rosa, Phys. Rev., vol. 9, p. 214; 1899.
23. Atwater and Snell, J. Am. Chem. Soc., vol. 25, p. 659; 1903.
24. Emery and Benedict, Amer. J. Physiology, vol. 28, p. 301; 1911.
25. Dickinson, B. S., Bull., vol. 11, p. 189; 1915.

WASHINGTON, November 18, 1931.

A CLOCK-CONTROLLED CONSTANT-FREQUENCY GENERATOR

By A. B. Lewis

ABSTRACT

A synchronous motor generator set is described in which the motor is forced to rotate in synchronism with signals from a standard clock circuit. This result is obtained by first running a specially wound motor synchronously from a 3-phase commercial power line. The field of this synchronous motor is then electrically rotated about the motor frame by an amount which exactly compensates for the departure of the frequency of the cmmercial power from true 60 cycles. This rotation of the motor field is produced by a rotary synchroscope which is in turn controlled by thyratron tubes, the grids of which are excited by a clock-driven tuning fork. The output of the generator is used to operate cycle counters, synchronous timers, or other light synchronous machinery.

The possibilities and limitations of the machine are discussed and data are given to indicate the accuracy (± 0.004 second) which may be expected from the machine when used as a timing device. Safety devices are described which shut down the machine should it for any reason fall out of synchronism with the clock signals or hunt excessively. The machine has an ultimate load capacity of 4 kw, and can take a suddenly applied load of 2 kw without serious hunting.

CONTENTS

	Page
I. Introduction	141
II. Description of apparatus	143
1. Source of true 60 cycles	143
2. The synchroscope	145
3. The synchronous motor generator	146
III. Operation	147
1. Operation of the device as a whole	147
2. The accuracy of the machine	148
3. Protective devices	150
4. Possible improvements	151
IV. Application	151
V. Appendix	153

I. INTRODUCTION

Methods for accurately measuring time intervals are always of interest in laboratory work. This is particularly so in laboratories where such instruments as frequency meters and watthour meters are tested. The large number of observations necessary in work of this character, as well as the necessity of holding power or frequency constant during the measured time interval, makes it imperative that the time consumed by each individual observation be as short as is consistent with accuracy. The need thus arises for a timing device which will permit an accuracy in time measurements of at least 1 part in 10,000 over a reasonably short interval of time. Such a device should be capable of operating continuously and reliably over con-

siderable intervals of time without attention. It should preferably have a sufficiently large load capacity to supply simultaneously a number of separate laboratories with time signals and to be reasonably unaffected by sudden large changes in load.

The nature of these requirements reduces considerably the number of types of devices available. The use of stop watches can be ruled out immediately both because of their uncertain starting and stopping error and because of their well-known fragility.[1] For some time the timing device used in making watthour meter tests at the Bureau of Standards has been a 20-cycle, clock-driven, tuning fork. A contact on this fork is arranged to close an electrical circuit and thus operate a cycle counter. Such an arrangement has two serious disadvantages. Each failure of the fork to completely close the circuit, as a result of dirty or poorly adjusted contacts, introduces a direct error into the observations. In addition, only a small amount of power can be drawn through such a contact.

These limitations would be avoided by the use of a rotating device which is forced to maintain a rotary motion of constant angular velocity. This device could be used to drive an alternator for the production of alternating current of constant frequency. The use of rotating machinery maintained in synchronism with standard time signals from a tuning fork or similar device has two chief advantages. First, the relatively large amount of energy present as energy of rotation assures continuity of operation even though the control mechanism should momentarily fail to function. Second, it can be so arranged that the control mechanism, such as a tuning fork, is no longer forced to carry the entire operating current of the device.

Devices embodying some of these principles are on the market. None are available, however, which have the high load capacity which it was desired to obtain from the machine to be described here. A synchronous motor-generator set having an ultimate capacity of 4 kw was, therefore, designed to operate in synchronism with time signals from a clock-controlled tuning fork. The principle upon which this machine operates is briefly as follows:

The rotor of a synchronous motor running synchronously from a supply line turns with respect to its d. c. magnetic field at an angular velocity determined solely by the frequency of the a. c. supply. If it is possible to rotate this d. c. magnetic field with respect to some stationary reference frame—that is, with respect to the stationary motor frame—the rotor of the synchronous motor will be forced to rotate with respect to this stationary frame at an angular velocity corresponding to the algebraic sum of the angular velocity determined by the a. c. supply frequency and the angular velocity of the d. c. magnetic field. In the machine described here the field coils of the synchronous motor are so wound and connected to an external commutator that a rotation of the commutator brushes produces a rotation of the magnetic field about the stationary motor frame. Means are then provided for rotating these commutator brushes, and hence the magnetic field of the motor, at an angular velocity directly proportional to the algebraic difference between true 60 cycles and the a. c. supply frequency. The rotor of the synchronous motor is thus forced to rotate, with respect to the stationary motor frame, at an angular

[1] A. L. Ellis, The Limitations of the Stop Watch as a Precision Instrument, Trans. Am. Inst. Elec. Eng., vol., 40, pp. 479–502; 1921.

velocity directly proportional to true 60 cycles. The device thus consists of the following essential parts: A source of true 60 cycles, consisting in this case of two thyratron tubes operating in an inverter circuit excited by a clock-controlled tuning fork; a synchroscope or device for producing the proper rotation of the commutator brushes mentioned above; and a specially wound synchronous motor-generator set.

The use of such a rotating magnetic field was originally suggested by H. B. Brooks, of this bureau, who had, many years ago, demonstrated experimentally the feasibility of such an arrangement. Most of the credit for the early development work in connection with the present apparatus should go to R. D. Wyckoff, formerly of this bureau. Mr. Wyckoff is responsible, in particular, for the design of the specially wound synchronous motor now in use. Mention should also be made of the contributions of V. E. Whitman, formerly of this

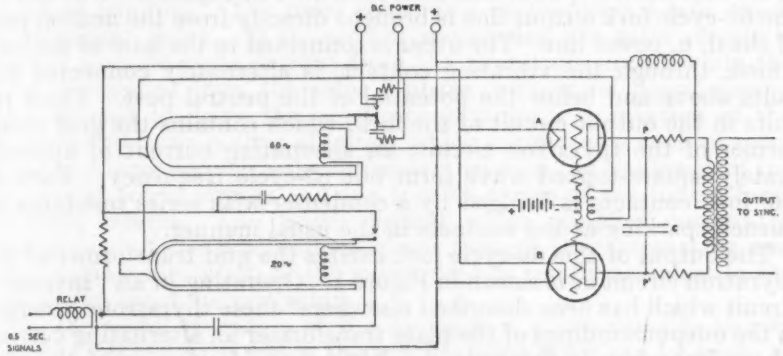

FIGURE 1.—*Schematic diagram of the clock-controlled tuning-fork circuit and the thyratron inverter circuit*

bureau, and others who have worked with the apparatus at various times.

II. DESCRIPTION OF APPARATUS

1. SOURCE OF TRUE 60 CYCLES

A chronometer made by Mercer, of London, serves as the primary time standard of this device. As certified by the time section of this bureau, this chronometer has a mean daily rate of −0.8 second at 20° C. where the minus (−) sign indicates that the chronometer is gaining time. The pallet fork of this chronometer is equipped with a contact which can be used to actuate an external relay. A comparison of this contact against a standard half-second pendulum in the manner described by Moon [2] indicated that this pallet fork could be relied upon to repeat its contact at half-second intervals to within one or two thousandths of a second.

The chronometer relay furnishes half-second impulses to the drive magnet of a 20-cycle fork by means of the usual arrangement which utilizes a condenser discharge. Figure 1 is a schematic diagram of

[2] Charles Moon, A Precision Method of Calibrating a Tuning Fork by Comparison with a Pendulum, B. S. Jour. Research, vol. 4, pp. 213-219; 1930.

the tuning-fork and thyratron circuits. The 60-cycle fork is driven in turn by impulses taken from a single-spring contact operated by the 20-cycle fork as is indicated in the same figure.

The steel forks were obtained from the Cambridge Instrument Co. Unfortunately the addition of the spring contacts altered the period of each fork sufficiently to necessitate the addition of small tuning weights. This, however, is not a serious matter, since the forks are not depended upon to maintain their calibrations, but are forced to vibrate in synchronism with signals from the standard clock. For this reason it has not been found necessary to provide a constant-temperature inclosure for the forks.

The output of the 60-cycle fork is obtained from a double spring contact on one prong of the fork. This contact vibrates between two stationary spring contacts which are insulated from each other and from the base and connected, respectively, to the (+) and (−) sides of a 230-volt d. c. power line as is indicated in Figure 1. One side of the 60-cycle fork output line is brought directly from the neutral post of the d. c. power line. The other is connected to the base of the fork which, through the vibrating contact, is alternately connected 115 volts above and below the potential of the neutral post. There results in the output circuit of the fork, which contains the grid transformer of the thyratron circuit, an alternating current of approximately square-topped wave form but 60-cycle frequency. Each of the fork contacts is bridged by a condenser with series resistance to quench sparking at the contacts in the usual manner.

The output of this 60-cycle fork excites the grid transformer of the thyratron circuit as is shown in Figure 1. Operating in an "inverter" circuit which has been described elsewhere[3] these thyratrons generate in the output windings of the plate transformer an alternating current whose frequency is determined solely by the frequency of the grid excitation.

The operation of the inverter circuit may be briefly described in the following manner: A 60-cycle voltage derived from the tuning fork is supplied to the grids of the tubes. (See fig. 1.) The magnitude of this voltage is just sufficient to overcome the grid bias battery and cause operation of the tubes. Suppose now that the grid of tube A has become positive, causing this tube to become conducting. A pulse of current flows through the plate transformer. The point P is now at a more negative potential than point P' and the condenser C receives a corresponding charge. On the next peak of the grid voltage wave the grid of tube B becomes positive and tube B becomes conducting. The condenser C now discharges through the resistance and the transformer coils. If the resistances and capacitances have been properly chosen, the negative potential built up at P during the finite duration of this discharge will be sufficient to make the plate of A momentarily negative with respect to its cathode and thus stop the discharge through A. A pulse of current now flows through tube B, and through the transformer in a direction opposite to that of the first pulse. These operations repeat themselves as long as the alternating grid supply is maintained. It is obvious that the frequency of the current in the output transformer will always be identical with that of the grid supply.

[3] W. R. G. Baker, A. S. Fitzgerald, and C. F. Whitney, Electron Tubes in Industrial Service, Electronics, vol. 2, pp. 581–583; 1931.

The current through the tuning-fork contacts when used in this circuit is of the order of 10 milliamperes. The average plate current through the thyratrons, FG–37, is of the order of 2.0 to 2.5 amperes. This current gives a drop of about 60 volts across the low-side coils of the plate transformer which is connected 360/60. This plate transformer supplies the rotor circuit of the synchroscope with an alternating current of true 60-cycle frequency.

2. THE SYNCHROSCOPE

The synchroscope is essentially a motor designed to operate at a speed and in a direction corresponding to the difference in frequency between the current supplied to its rotor and the current supplied to its stator system. Such a rotary synchroscope has been described in some detail by Lincoln.[4] In the machine used here the stator is provided with a 3-phase, 4-pole, 110-volt, Y-connected, standard polyphase winding. The rotor contains a single-phase 4-pole winding on salient poles. In its present application the rotor circuit is supplied with 60-cycle current from the thyratron circuit while the stator is supplied from the same 3-phase commercial power supply which is used to drive the synchronous motor. A rotation of the synchroscope rotor is thus obtained which corresponds both in magnitude and direction with the difference between the frequency of the commercial power supply and the true 60 cycles of the tuning-fork-thyratron circuit. The brush rigging which supplies current to the d. c. field of the synchronous motor through its commutator, and thus produces a rotation of the motor field, is rigidly attached to the shaft of the synchroscope rotor.

The successful operation of the device as a whole depends largely upon the fidelity with which the synchroscope rotor can be made to follow the variations in frequency of commercial power. It thus becomes necessary to consider the equation for the torque acting on the synchroscope rotor and the equation of motion for the synchroscope rotor itself.

The current and torque equations and the equation of motion of the synchroscope rotor are given as equations (8), (9), and (11), respectively, in the Appendix. It is apparent from equations (8) and (9) that the component of torque tending to produce the desired rotation of the rotor; that is, $2K\,AD \sin [(\omega_2-\omega_1)t-\beta-\theta_1]$, is produced by the interaction of the two currents flowing as the direct result of the applied rotor and stator voltages. The torque equation and the equation of motion indicate that the effect of the induced components of current in the rotor and stator circuits is to produce a double frequency disturbance in the motion of the synchroscope rotor. These induced components of current are, therefore, suppressed by increasing both the stator and rotor impedances. The stator voltage is raised to 480 volts and the stator impedance, per phase, is increased to approximately 800 ohms by means of external choke coils. Similarly, the rotor voltage is raised to approximately 360 volts and the rotor impedance to approximately 700 ohms. These precautions reduce the induced-current components of equation (8) to magnitudes

[4] P. M. Lincoln, Synchronism and Frequency Indication, J. Am. Inst. Elec. Eng., vol. 18, pp. 265–270; 1901.

not more than 0.1 those of the main current components $E_rA \cos (\omega_1 t - \gamma)$ and $E_sD \cos (\omega_2 t - \alpha - \zeta)$.

As an additional precaution the induced-current component $E_iC \cos (\omega_2 t - \beta - \alpha - \delta)$ is still further suppressed in the following manner: If the synchroscope rotor is stationary, the frequency of this induced component of rotor current will be $\omega_2/2\pi$, which is the same as the commercial frequency and which is the same as the frequency of the generator output when the motor is running synchronously from the line. If, however, the synchroscope is rotating at its proper velocity, $(\omega_2 - \omega_1)$, the frequency of this component will be $\frac{\omega_2 - (\omega_2 - \omega_1)}{2\pi}$ or $\omega_1/2\pi$. This again is the frequency of the generator output since under these conditions the motor will be running in synchronism with the tuning fork whose frequency is $\omega_1/2\pi$. It thus appears that under all steady operating conditions the frequency of the induced current component in the synchroscope rotor will be the same as the frequency of the generator output. A voltage may, therefore, be taken from the generator output having such a magnitude and phase that, when introduced into the rotor circuit of the synchroscope, it completely supresses the current component $E_sC \cos (\omega_2 t - \beta - \alpha - \delta)$.

In addition to the double-frequency disturbance there are present in the motion of the synchroscope rotor, as is shown in equation (9), the damped free vibrations of the system acting as a torsion pendulum. If the motion of the synchroscope rotor under the influence of its main driving torque was strictly uniform, that is, if $(\omega_2 - \omega_1)$ was constant with time, these free vibrations would be damped out quickly. Such, however, is not the case. The commercial frequency actually varies slightly but continually. As a result, the motion of the synchroscope rotor consists of a slow but irregular rotation, the rotor frequently coming to a complete stop. Some damping must, therefore, be present. It is also important that the free period of the system be large in comparison with the period of these variations of the line frequency and in comparison with the free period of the motor-generator set (approximately 0.5 second). To this end an iron flywheel has been attached to the rotor shaft, giving the rotor system a moment of inertia of approximately 2.3×10^5 g–cm^2. With the maximum torques developed in the synchroscope, approximately 500 g–cm, the system has a minimum free period of about four seconds. This moment of inertia reduces to a negligible amount the response of the rotor system to the double-frequency components of torque. It is found, in addition, that the friction of the commutator brushes is sufficient to satisfactorily damp out the transient terms in the equation of motion of the synchroscope.

Under these conditions the synchroscope, once pulled into step, will satisfactorily operate over a frequency difference, $(\omega_2 - \omega_1)$, of ± 2.5 cycles. This gives an ample margin of safety since the commercial frequency in Washington is normally within a few tenths of a cycle of true 60 cycles.

3. THE SYNCHRONOUS MOTOR-GENERATOR

The synchronous motor now in use was obtained by modifying a 7.5-horsepower, 60-cycle, 3-phase, 440-volt induction motor which had a wound rotor. In its present application the motor action is inverted;

that is, 3-phase a. c. power is supplied to the rotor, and the stator coils, which have been rewound and brought out to an external commutator, are excited with direct current for synchronous operation. The rotor winding is the original factory winding. From data obtained on the original stator winding when connected as a completely distributed 4-pole d. c. field, a new stator winding was designed to give normal excitation from a 120-volt d. c. supply. The final stator winding consists of 59 coils having 72 turns of No. 21 A. W. G. single-silk-enamel wire per coil. The double-layer wave winding using diamond-shaped coils as ordinarily used in induction-motor stator windings was adopted. The coils were connected in the same manner as a d. c. motor armature having a 4-pole 2-circuit winding, and the leads brought out for connection to a 59-bar commutator. A rotation of the commutator brushes therefore produces an actual rotation of the d. c. magnetic field about the stator frame.

In its normal operation the motor is constantly subjected to torsional impulses and disturbances as a result of the continual shifting of its d. c. magnetic field about the stator frame. It is important, therefore, to have the machine heavily damped. For this reason the damping winding was made as heavy as the available space permitted. Reactors, each having an impedance of approximately 2 ohms at 60 cycles, have been placed in series with the rotor. Finally, the motor is run very much underexcited. It is possible to materially reduce the frequency of the hunting of the machine, but not necessarily the amplitude of the hunting, by the addition of a heavy flywheel to the rotor shaft. The presence of such a flywheel makes it necessary to provide some external means; that is, other than the torque of the currents induced in the damping windings, of bringing the motor up to synchronous speed. The machine is, therefore, not provided with a flywheel.

A 3-phase, 4-kw, 60-cycle generator is directly coupled to the shaft of the synchronous motor. This generator constitutes a source of true 60 cycles which can be used to operate cycle counters, synchronous timers, small synchronous motors, or other similar devices. In addition to its a. c. windings, the generator is provided with a commutator and d. c. windings of sufficient capacity to provide the excitation of the generator field and synchronous motor field should this become desirable.

Figure 2 is a diagrammatic sketch of the connections used in the set-up. Figures 3 and 4, respectively, are photographs of the assembled tuning-fork-thyratron apparatus and the motor-generator set itself.

III. OPERATION

1. OPERATION OF THE DEVICE AS A WHOLE

The operation of the device as a whole proceeds as follows: The synchronous motor is brought up to speed with the induction-motor torque of its damping winding and is synchronized with the commercial a. c. power line. The synchroscope stator is excited from the same commercial a. c. power line. The generator field is excited and a voltage is taken from the generator output having the proper phase and magnitude to exactly neutralize the induced voltage component in the rotor circuit of the synchroscope. The tuning fork and thyratron circuits are then put into operation and the output of the thyratron

circuit introduced into the synchroscope rotor. The synchroscope rotor then rotates, and with it the synchronous motor field. Under these conditions, as has been explained above, the synchronous motor is forced to rotate at a speed corresponding to the frequency of the tuning-fork supply, which is 60 cycles. The output of the generator may now be used for any purposes which call for a current of true 60 cycles, averaged over as much as a few seconds.

Experiment has shown that the machine can safely take a suddenly applied load of as much as 2 kw without excessive hunting.

2. THE ACCURACY OF THE MACHINE

In its use as a timing device the apparatus is subject to two major sources of error. First, even if the motor could be so adjusted as to

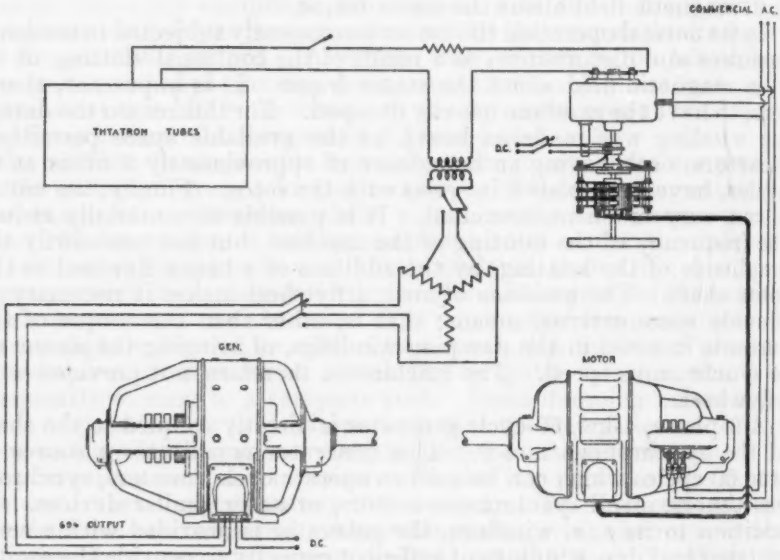

FIGURE 2.—*Schematic wiring diagram of the clock-controlled synchronous motor-generator set*

maintain precisely and without hunting its exact synchronism with the 60-cycle fork, and thus with the signals from the chronometer, its time signals could never be more reliable than those of the chronometer. The daily rate of this chronometer is, as has been stated, of the order of -0.8 second a day. This amounts to a systematic error of about 1 part in 100,000, and is therefore entirely negligible for all the purposes for which this generator will be used. Second, the motor does not actually, from instant to instant, maintain exact synchronism with the 60-cycle fork, but is continually hunting about this synchronous position. To obtain a quantitative estimate of the error introduced by this hunting, the following experiment was performed:

A stroboscope was set up which consisted of a neon lamp lighted by the 60-cycle fork output and viewed through a slotted disk on the end of the generator shaft. The hunting of the machine then became apparent as an oscillation through a small angle of the resulting bright

FIGURE 3.—*Photograph of the assembled tuning-fork-thyratron apparatus*

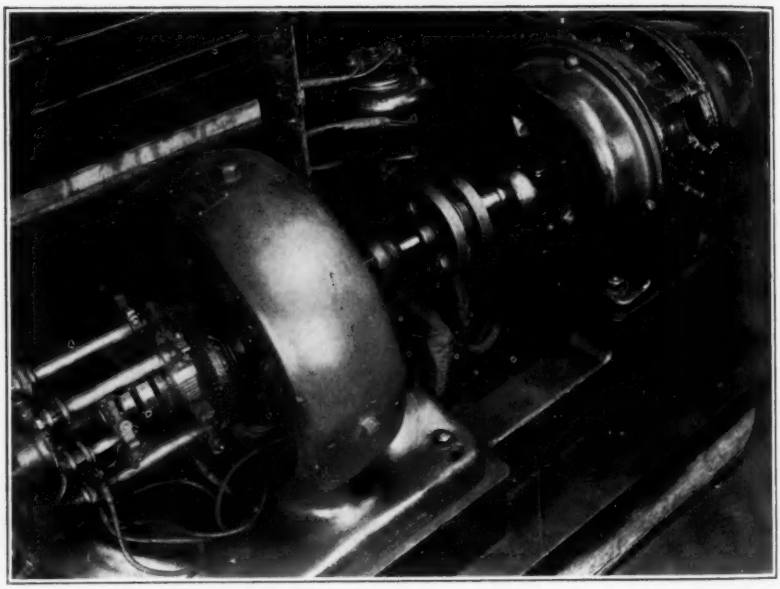

FIGURE 4.—*Photograph of the complete clock-controlled motor-generator set and synchroscope*

slit image. The instantaneous position could be determined with a protractor placed behind the slotted disk. The neon lamp circuit was arranged to be closed approximately once every three seconds, and the instantaneous position of the generator shaft was read and recorded for each flash of the neon lamp. Over 1,300 individual observations were made, spread over a total interval of approximately five hours. The resulting observations were averaged and plotted, after the fashion of an ordinary error function, as probability against departure from the mean. These data are plotted in Figure 5 in which the deviation from the mean in mechanical degrees has been reduced to the resulting error in time, Δt, in thousandths of a second. Since the generator shaft is turning at the rate of 10,800 mechanical de-

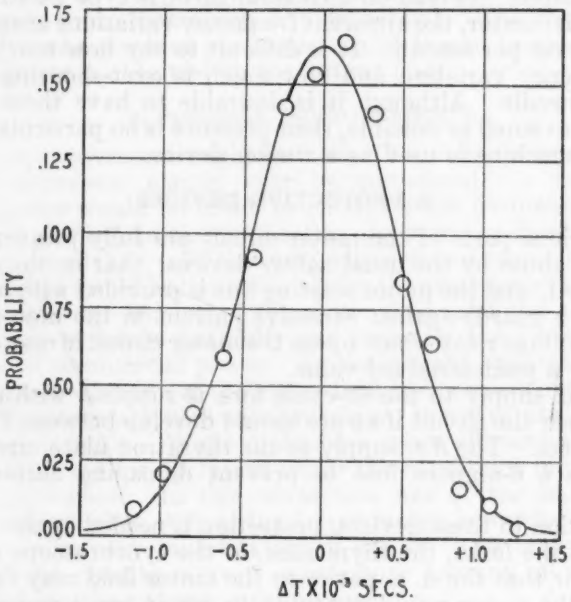

FIGURE 5.—*Probability of a given error in time measurement introduced by the random hunting of the machine*

O, observed points; —, plotted from the equation $y=0.162e^{-(1.56\Delta t)^2}$; Δt in thousandths of a second.

grees per second, 10.8 mechanical degrees correspond to 0.001 second. The solid curve in Figure 5 represents the probability equation

$$y = 0.162e^{-(1.56\Delta t)^2}$$

where

y is the probability.

Δt is the amount by which the machine is away from its mean position expressed in thousandths of a second.

The constant for this curve was obtained from the experimental data by means of Peter's rule. The probable error of the machine, computed from this equation, is ± 0.0003 second. Similarly, it can be verified that the probability that the machine will be within ± 0.002 second of its mean position at any instant is 0.99998.

It is to be noted that this error is a truly random one and is not cumulative. When time intervals of any appreciable length are being measured, say 50 or 100 seconds, this random error becomes entirely negligible.

A safety device, to be described in the next section, is provided which definitely shuts down the machine if, for any reason, this instantaneous hunting error amounts to more than a predetermined amount, say, ± 0.004 second.

Since the free period of the motor-generator set is fairly short, being something less than 1 second, the variations in angular position taking place as a result of the hunting of the machine occur with considerable rapidity. Consequently the variations in instantaneous frequency are appreciable. As read on a General Electric type P3 tuned-circuit frequency indicator, the apparent frequency variations are of the order of ± 0.1 cycle per second. It is difficult to say how much of this is true frequency variation and how much is over-shooting of the instrument needle. Although it is desirable to have these frequency variations as small as possible, their presence is no particular handicap when the machine is used as a timing device.

3. PROTECTIVE DEVICES

The various parts of the motor circuit are fully protected against accidental abuse by the usual safety devices; that is, the a. c. power line is fused, and the motor starting box is provided with an overload relay which guards against excessive current in the motor armature and a no-voltage relay which opens the motor circuit in case the voltage falls below a predetermined value.

The d. c. supply to the 60-cycle fork is supplied with a 2-ampere relay to clear the circuit if an arc should develop between the 60-cycle fork contacts. The d.c. supply to the thyratron plate circuit is supplied with a 6-ampere fuse to prevent damaging currents in this circuit.

In addition to these devices, protection is needed against the possibility that the forks, the thyratrons, or the synchroscope may fail to function, or that the d. c. power to the motor field may fail. In the first case the motor would continue to run in synchronism with the line frequency without damage to itself, but as a timing device it would no longer be reliable. In the second case the motor would continue to run as an induction motor on the torque arising from the damping windings. As a timing device it would no longer be accurate, and the motor itself would be subject to injury, because of the small load capacity of the damping winding. Some precaution must also be taken against excessive hunting on the part of the motor.

To take care of these possibilities a differential relay was constructed. This relay is mechanically similar to an ordinary telegraph relay, except that the core and armature are laminated. One of the two coils on this relay is excited from the true 60-cycle source in parallel with the synchroscope rotor. The other coil on the relay is excited from the generator output. Each of these coils contains 7,000 turns of No. 33 A. W. G. silk-enamel wire and draws a current of approximately 75 milliamperes. When the generator is running in synchronism with the fork, these voltages are so chosen and adjusted that the magnetizing forces from the two coils aid each other. The spring tension on the armature of the relay is then adjusted until the re-

sultant force from the two coils is just sufficient to hold the relay armature in place. If, for any reason, either of these two sources of excitation should fail, or if, for any reason, the generator voltage should swing out of phase with respect to the fork voltage, as by excessive hunting, by more than a predetermined amount, the relay armature will be released. The releasing of the relay armature closes a by-pass which short-circuits the magnet coils of the no-voltage relay of the starting box and shuts down the synchronous motor. The relay can be adjusted conveniently to release on a phase displacement of the motor of about 40 mechanical degrees from its mean position. This corresponds to about ± 0.004 second or about a quarter of a cycle. This adjustment allows the ordinary and unavoidable hunting of the machine to take place and yet guards definitely against an error amounting to more than about ± 0.004 second. The observer is also assured that the machine is running properly and in synchronism as long as voltage is obtained on the output lines.

4. POSSIBLE IMPROVEMENTS

Several improvements might be made if the construction of a similar piece of apparatus should ever be considered. A more heavily damped motor would do much to eliminate the frequency variations now taking place. In this connection the mercury flywheel suggests itself as a possibility. With a critically damped motor the accuracy of the machine would be limited solely by the accuracy of the chronometer, the finite subdivision of the motor field, and the ability of the synchroscope to follow faithfully and instantly the variations in the frequency of commercial power. In the present apparatus the effect of the finite subdivision of the motor field has been entirely negligible. In a more accurately controlled machine, however, its effect might become appreciable. Without doubt a more efficient synchroscope could be designed for operation under the conditions imposed by the present application. In this connection one of the small indicator motors on the market, such as the Selsyn motor, is worthy of consideration. A preliminary investigation of one of these motors indicated that it would develop a very satisfactory amount of torque when substituted for the present synchroscope.

The spring contacts now in use on the tuning forks were installed at a time when it was necessary to draw a rather heavy current through these contacts. The thyratron grid circuit requires so little current that this particular difficulty is now avoided. It should, therefore, be possible to use platinum wire contacts dipping in mercury wells. Such contacts have much less effect on the period of the fork than the ones now in use.

IV. APPLICATIONS

The output of the machine described here may be used to operate cycle counters, synchronous timers, or any of the other electrical timing devices on the market. A synchronous clock or timer operating from the a. c. output of this machine can be relied upon to keep the time of the master chronometer over a period of as much as 4 or 5 seconds or longer with a probable error of ± 0.0003 second and a maximum error of ± 0.004 second. These errors are far smaller then can be detected on commercial synchronous timers, most of which can be read to only 0.01 second. The output of the machine

may also be used to operate small synchronous motors driving chronographs or other synchronous machinery whose average speed, taken over a period of 4 or 5 seconds, must be constant to a high degree of precision.

The unique characteristic of the machine is its large load capacity. Although possessing the inherent accuracy of the master chronometer, the machine can take a suddenly applied load of 2 kw and is capable of carrying a continuous load of 4 kw without injury to itself. There are no serious limitations on the size of such a machine. The high accuracy of the machine, its large load capacity, and the automatic protective devices which can be used with it, make it particularly adapted to installations where a large number of laboratories must be supplied with time signals.

This apparatus was primarily designed for, and finds its greatest use in, the measurement of short-time intervals in the routine calibration of commercial instruments, such as watthour meters and frequency meters. The necessity of holding watts or frequency constant during the time interval measured makes it imperative that that time interval be as short as is consistent with accuracy. Commercial impulse counters and synchronous timers are used to measure these intervals, the accuracy of the measurement being limited at present solely by the accuracy of the recording device. With such instruments it is possible to measure time intervals of 10 seconds with an accuracy of 1 part in 1,000 and intervals of 100 seconds with an accuracy of 1 part in 10,000. These limits represent a marked improvement over the accuracy obtained when synchronous timers are used directly on a commercial line. It is well known [5] that even in systems where the frequency is closely controlled and averages 60 cycles to a high degree of precision over long intervals of time, the instantaneous frequency can not be relied upon to more than about 1 part in 600 over short intervals of time. The accuracy of the present machine is such that it would justify the use of a more precise instrument for recording these time intervals than is now commercially obtainable.

In calibrating frequency meters in the neighborhood of 60 cycles, it is possible to use an impulse counter to count the electrical beats between the unknown frequency and the true 60 cycles of this generator and measure the corresponding time interval. This method leads to a considerable saving in time and increase in accuracy in the measurement as compared with the usual method of counting cycles directly and measuring the corresponding time interval.

The installation of a 1,000-cycle generator on the shaft of this motor-generator set would furnish a convenient source of 1,000-cycle current, of controlled frequency, for use in routine bridge measurements about the laboratory.

In addition to these applications, the apparatus should find use in the Bureau of Standards in driving the small synchronous motors used in timing exposures in photographic research, and in measuring short-time intervals in X-ray and radio-activity work.

A device similar in principle to that described here may find use in the maintenance of isochronism in small motors such as is necessary

[5] J. M. Adams, Time Measuring by Commercial Alternating Current with Controlled Frequency, J. Opt. Soc. Am., vol. 19, pp. 384–386, 1929.

in the operation of machine telegraph systems.[6] A similar application may be found in the operation of radio direction-finding apparatus. It is stated[7] that in such installations it is not only necessary to operate two stations in exact synchronism, but also to rotate the loop antennas at a velocity of 1 revolution per minute with such uniformity that the loop shall never be more than 1 degree from its proper position. With a synchronous motor running from the machine described here and driving a suitable reduction gear to give 1 revolution per minute, one could be assured that the final rotating member would never be more than ± 0.02 degree from its proper position.

V. APPENDIX. DERIVATION OF THE EQUATION OF MOTION OF THE SYNCHROSCOPE

Consider a synchroscope with a symmetrical 3-phase stator and a single-phase rotor. The position of the rotor in space is defined by the angle β, measured from an initial line determined by the position of maximum mutual inductance between the rotor coil and stator coil a. Since the mechanical frequency of rotation of the synchroscope rotor will always be very small compared to the frequency of alternation of the supply currents, we shall neglect the currents induced by this mechanical rotation. That is to say, we shall neglect terms of the order $d\beta/dt$. We thus treat M, the mutual inductance between the rotor and stator circuits, as a function of β and hence of t (since β is the explicit function of t which we wish to find), but neglect terms of the order dM/dt. We assume that the mutual inductances between the rotor coil and the successive coils of the 3-phase stator system can be expressed as sinusoidal functions of the angle β.

With these assumptions in mind, let the rotor circuit alone be excited, the stator coils being closed through circuits of normal impedance, but with no applied emf. The equations for the resulting instantaneous voltages are

$$\begin{aligned} &\frac{d}{dt}[Li_r + M_a i_a + M_b i_b + M_c i_c] + Ri_r = e_r \\ &\frac{d}{dt}[\mathrm{M}_k i_r + Ni_k] + Si_k = 0,\ k = a,\ b,\ c. \end{aligned} \tag{1}$$

where

e_r is the instantaneous applied rotor voltage.
i_r is the instantaneous rotor current.
i_a, i_b, and i_c are the instantaneous currents in stator phases a, b, and c, respectively.
R is the resistance of the rotor circuit in ohms.
S is the resistance of each stator phase in ohms.
L is the self-inductance of the rotor circuit in henries.
N is the self-inductance of each stator phase in henries.
M_a, M_b, and M_c are the mutual inductances, in henries, between the rotor coil and stator coils a, b, and c, respectively.

[6] H. H. Harrison, Developments in Machine Telegraph Systems and Methods of Operation, J. Inst. Elec. Eng. (London), vol. 69, pp. 1369–1453; 1930.
[7] N. F. S. Hecht and D. P. Alexander, A Device for Maintaining Isochronism in Low-Power Electric Motors, J. Inst. Elec. Eng. (London), vol. 69, pp. 83–88; 1930.

Now make the usual substitutions defined by the real parts of the following exponentials:

$$\begin{aligned} e_r &= E_r e^{j\omega_1 t} \\ i_r &= G e^{j\omega_1 t} \\ i_a &= H \cos \beta e^{j\omega_1 t} \end{aligned}$$

$$i_b = H \cos \left(\beta - \frac{2\pi}{3}\right) e^{j\omega_1 t} \tag{2}$$

$$i_c = H \cos \left(\beta - \frac{4\pi}{3}\right) e^{j\omega_1 t}$$

where

E_r is the maximum value of the applied rotor voltage.

G is the maximum value of the current in the rotor circuit.

H is the maximum value of the current in each stator coil.

j is the imaginary operator $\sqrt{-1}$.

ω_1 is $2\pi \times$ the frequency of the applied rotor voltage.

Finally, assume

$$\begin{aligned} M_a &= M_o \cos \beta \\ M_b &= M_o \cos (\beta - 2\pi/3) \\ M_c &= M_o \cos (\beta - 4\pi/3) \end{aligned} \tag{3}$$

Substitution of equations (2) and (3) in equation (1) leads to the following linear equations which serve to determine G and H:

$$(R + j\omega_1 L)G + \frac{3}{2}(j\omega_1 M_o)H = E_r \tag{4}$$

$$j\omega_1 M_o G + (S + j\omega_1 N)H = 0$$

The complex values for G and H obtained from equations (4) are to be substituted in equations (2) and the real parts of the resulting currents retained.

These operations lead to current equations of the following forms, for the case of rotor excitation alone:

$$\begin{aligned} i_r &= E_r A \cos (\omega_1 t - \gamma) \\ i_a &= E_r B \cos \beta \cos (\omega_1 t - \varepsilon) \\ i_b &= E_r B \cos \left(\beta - \frac{2\pi}{3}\right) \cos \left(\omega_1 t - \varepsilon - \frac{2\pi}{3}\right) \\ i_c &= E_r B \cos \left(\beta - \frac{4\pi}{3}\right) \cos \left(\omega_1 t - \varepsilon - \frac{4\pi}{3}\right) \end{aligned} \tag{5}$$

where

A and B are constants, determined by the circuit constants, having the dimensions of admittance.

γ and ε are phase angles determined by the circuit constants.

Consider now the case in which the stator coils are excited from a 3-phase source, the rotor being closed through a circuit of normal

impedance, but with no applied emf. The equations for the resulting instantaneous voltages are—

$$\frac{d}{dt}[Li'_r + M_a i'_a + M_b i'_b + M_c i'_c] + Ri'_r = 0 \tag{6}$$

$$\frac{d}{dt}[M_k i'_r + N i'_k] + S i'_k = E_k,\ k = a,\ b,\ c$$

where the symbols have the same meanings as in equation (1), the currents in this case being distinguished from those in equation (1) by primes.

Following a procedure analogous to that used in the solution of equation (1), we obtain for the currents, equations of the following forms:

$$\begin{aligned}
i'_r &= E_s C \cos(\omega_2 t - \alpha - \beta - \delta) \\
i'_a &= E_s D \cos(\omega_2 t - \alpha - \zeta) + E_s F \cos\beta \cos(\omega_2 t - \alpha - \beta - \eta) \\
i'_b &= E_s D \cos\left(\omega_2 t - \alpha - \zeta - \frac{2\pi}{3}\right) + E_s F \cos\left(\beta - \frac{2\pi}{3}\right)\cos\left(\omega_2 t - \alpha - \beta - \eta - \frac{2\pi}{3}\right) \\
i'_c &= E_s D \cos\left(\omega_2 t - \alpha - \zeta - \frac{4\pi}{3}\right) + E_s F \cos\left(\beta - \frac{4\pi}{3}\right)\cos\left(\omega_2 t - \alpha - \beta - \eta - \frac{4\pi}{3}\right)
\end{aligned} \tag{7}$$

where

E_s is the maximum value of the applied stator voltage.

C, D, and F are constants determined by the circuit constants and having the dimensions of admittance.

δ, ζ, and η are phase angles determined by the circuit constants.

ω_2 is $2\pi \times$ the frequency of the applied stator voltage.

α is the initial phase angle existing between the applied rotor and stator voltages.

Since under normal operating conditions both stator and rotor circuits are excited from separate sources, we obtain the complete expressions for the currents flowing in these circuits under normal operating conditions by adding equations (5) and (7).

$$\begin{aligned}
I_r &= E_r A \cos(\omega_1 t - \gamma) + E_s C \cos(\omega_2 t - \alpha - \beta - \delta) \\
I_a &= E_r B \cos\beta \cos(\omega_1 t - \varepsilon) + E_s D \cos(\omega_2 t - \alpha - \zeta) + E_s F \cos\beta \cos(\omega_2 t - \alpha - \beta - \eta) \\
I_b &= E_r B \cos\left(\beta - \frac{2\pi}{3}\right)\cos\left(\omega_1 t - \varepsilon - \frac{2\pi}{3}\right) + E_s D \cos\left(\omega_2 t - \alpha - \zeta - \frac{2\pi}{3}\right) \\
&\quad + E_s F \cos\left(\beta - \frac{2\pi}{3}\right)\cos\left(\omega_2 t - \alpha - \beta - \eta - \frac{2\pi}{3}\right) \\
I_c &= E_r B \cos\left(\beta - \frac{4\pi}{3}\right)\cos\left(\omega_1 t - \varepsilon - \frac{4\pi}{3}\right) + E_s D \cos\left(\omega_2 t - \alpha - \zeta - \frac{4\pi}{3}\right) \\
&\quad + E_s F \cos\left(\beta - \frac{4\pi}{3}\right)\cos\left(\omega_2 t - \alpha - \beta - \eta - \frac{4\pi}{3}\right)
\end{aligned}$$

The various current components may be identified in the following manner: The components $E_rA \cos(\omega_1 t-\gamma)$ and $E_sD \cos(\omega_2 t-\alpha-\zeta)$, etc., represent currents flowing in the rotor and stator circuits as the direct result of the applied rotor and stator voltages, respectively. They may be referred to as the "main" rotor and stator currents. The component $E_sC \cos(\omega_2 t-\alpha-\beta-\delta)$ represents a current induced in the rotor circuit by the components of stator current of frequency ω_2. Similarly, the components of stator current $E_rB \cos\beta \cos(\omega_1 t-\varepsilon)$, etc., represent currents induced in the stator system by the main component of rotor current. The components of stator current $E_sF \cos\beta \cos(\omega_2 t-\alpha-\beta-\eta)$, etc., represent currents induced in the stator system by the component of rotor current having a frequency ω_2; that is, by the "induced" rotor current. We may, therefore, speak of these last three current components as "induced" currents.

The torque is obtained in the usual manner by forming the products

$$T=\Sigma\, I_r I_s\, dM_s/d\beta,\ s=a,\ b,\ c$$

Products of sines are expanded into sums and differences of the corresponding angles and the sums, representing high frequency torques, are discarded. The resulting torque equation is of the following form:

$$\begin{aligned} T=K\Big[&2AD\sin\{(\omega_2-\omega_1)t-\beta-\theta_1\}-AF\sin\{(\omega_2-\omega_1)t+\beta-\theta_2\}\\ &-BC\sin\{(\omega_2-\omega_1)t-3\beta-\theta_3\}-\frac{E_r}{E_s}AB\sin\{2\beta-\theta_4\}\\ &-\frac{E_s}{E_r}CF\sin\{2\beta-\theta_5\}+2\frac{E_s}{E_r}CD\sin\theta_6\Big] \end{aligned} \tag{9}$$

where

K is a constant having the dimensions of (voltage)^2

θ_1, θ_2, θ_3, θ_4, θ_5, and θ_6 are constant phase angles.

As has been mentioned in the discussion of the synchroscope, the rotor and stator impedances have been increased to such an extent that the admittances C, D, and F are approximately 0.1 the magnitude of the admittances A and D, while the voltages E_r and E_s are of the same order of magnitude. The last five terms of the torque equation will, therefore, be small in comparison with the first.

Let us now set up the equation of motion of the synchroscope rotor

$$\begin{aligned} Id^2\beta/dt^2+kd\beta/dt=&A_1\sin\{(\omega_2-\omega_1)t-\beta-\theta_1\}+A_2\sin\{(\omega_2-\omega_1)t+\beta-\theta_2\}\\ &+A_3\sin\{(\omega_2-\omega_1)t-3\beta-\theta_3\}+A_4\sin\{2\beta-\theta'_4\}-A_5 \end{aligned} \tag{10}$$

where

β is the angle defining the position of the rotor in space as previously defined

I is the moment of inertia of the rotor system

k is the coefficient of damping of the system.

The other abbreviations made in the torque equation are obvious. It should be remembered that A_2, A_3, A_4, and A_5 are small compared with A_1.

We obtain an approximate solution, β_0, of equation (10) by neglecting the last four terms of the torque expression, and assuming that β is never far from its synchronous value $(\omega_2-\omega_1)t$. Equation (10) then readily reduces to the linear form with constant coefficients

arising from the forced vibrations of a harmonic oscillator. If β_0 is approximately $(\omega_2-\omega_1)t$ it is apparent that the last four terms in the torque expression in equation (10) reduce approximately to torques having a frequency $2(\omega_2-\omega_1)$. We find the effect of these disturbing double-frequency torques to a first approximation by assuming

$$\beta=\beta_0+\Delta\beta$$

substituting in equation (10), neglecting products and squares small quantities, and solving for $\Delta\beta$.

These operations lead to a solution for β of the following form:

$$\beta=(\omega_2-\omega_1)t-\phi$$
$$+e^{-\frac{kt}{2I}}[C_0\cos(2\pi\nu_0 t-\delta_0)+C_1\cos(2\pi\nu_1 t-\delta_1)] \qquad (11)$$
$$+C_2\sin[2(\omega_2-\omega_1)t-\delta_2]$$

where

$$2\pi\nu_0=\frac{[4IA_1-k^2]^{1/2}}{2I}$$

$$2\pi\nu_1=\frac{\left[4IA_1\cos\frac{k(\omega_2-\omega_1)}{A_7}-k_2\right]^{1/2}}{2I}$$

k^2 is less than $4IA$

C_0 and C_1 are amplitude factors depending upon the initial conditions

C_2 is an amplitude factor depending upon the magnitude of the disturbing torque, upon $1/I$ and $1/k$.

ϕ, δ_0, δ_1, and δ_2 are constant phase angles.

The motion of the synchroscope rotor, therefore, consists of a steady rotation at an angular velocity $(\omega_2-\omega_1)$, damped free vibrations of the system acting as a torsion pendulum, and undamped forced vibrations of a frequency $2(\omega_2-\omega_1)$.

WASHINGTON, November 11, 1931.

○